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Article

Synthesis, Characterization, and Electrochemical Properties of Bisosmabenzenes Bridged by Diisocyanides

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Treatment of osmabenzene $[Os(CHC(PPh_3)CHC(PPh_3)CH)Cl_2(PPh_3)_2]OH$ (**3**) with various diisocyanides in the presence of NH_4PF_6 afforded a series of diisocyanide-bridged bisosmabenzenes $[(\mu\text{-}CN{-}R{-}NC)\{Os(CHC(PPh_3)CHC(PPh_3)CH)Cl_2(PPh_3)\}_2][PF_6]_2$ (R = 4,4′-C_6H_4-C_6H_4 (**5a**), 4,4′-$C_6H_4CH_2C_6H_4$ (**5b**), 4,4′-$C_6H_4OC_6H_4$ (**5c**), 1,4-C_6H_4 (**5d**)) in good yields through ligand substitution reactions. Similarly, reaction of osmafuran $[Os(CHC(PPh_3)C(OEt)O)Cl_2(PPh_3)_2]$ (**6**) with 1,4-phenylenediisocyanide produced the diisocynide-bridged bisosmafuran $[\mu\text{-}(1,4\text{-phenylenediisocyanide})\{Os(CHC(PPh_3)C(OEt)O)Cl(PPh_3)_2\}_2]Cl_2$ (**7**). Bisosmabenzenes containing a chloro and a phosphonium substituent on each metallacycle $[(\mu\text{-}CN{-}R{-}NC)\{Os(CHC(PPh_3)CHCClCH)Cl(PPh_3)_2\}_2]Cl_2$ (R = 4,4′-C_6H_4-C_6H_4 (**9a**), 4,4′-$C_6H_4CH_2C_6H_4$ (**9b**), 4,4′-$C_6H_4OC_6H_4$ (**9c**), 1,4-C_6H_4 (**9d**)) could be obtained in modest yields from the reactions of the osmacycle $[Os(CH{=}C(PPh_3)CH(OH)\text{-}\eta^2\text{-}C{\equiv}CH)Cl_2(PPh_3)_2]$ (**8**) with corresponding diisocyanides in the presence of NH_4PF_6 and NaCl via nucleophilic addition reactions. All of these complexes have been fully characterized by ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectrometry, IR spectrometry, and elemental analyses. Moreover, the structure of **9d** has been established by X-ray crystallography. The electrochemical properties of stable bisosmabenzenes **9a**−**d** have been investigated, which revealed that the two metal centers in **9c** and **9d** can interact with each other through a diisocyanide bridge.

Introduction

Since the first stable transition metal-containing metallabenzene was reported in 1982 by Roper et al.,[1] impressive progress has been made in the chemistry of this interesting class of aromatic compounds both experimentally[2] and theoretically.[3] A number of stable metallabenzenes, including ruthenabenzenes,[4] osmabenzenes,[5] iridabenzenes,[6] platinabenzenes,[7] and other metallabenzenes,[8] have been successfully isolated and characterized in the past decades. However, studies of their physical properties are still rather

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limited to a few reports. During the course of our systematic investigation on the chemistry of metallabenzenes based on our facile approaches to construct aromatic metallacycles through cycloaddition of unsaturated C_5 building blocks with simple transition-metal complexes bearing phosphine ligands,[4d,5k,n] we have reported recently the electrochemical properties of a series of ruthenabenzenes and osmabenzenes.[5n,9,10] Importantly, it was found that there is electronic communication between the two metal centers in the trichloro-bridged bisruthenabenzenes[9] and bisosmanaphalenes.[10] Bismetallabenzenes and their analogues, although interesting, are extemely rare. To the best of our knowledge, the trichloro-bridged bisruthenabenzenes and bisosmanaphthalenes reported by our group represent the only examples up to now,[9,10] while the ruthenium complexes with two π-coordinated ruthenabenzene ligands reported by Salzer are bis(metallabenzene) π-complexes, which belong to metallabenzene sandwich compounds.[11] The lack of convenient methods to construct bismetallabenzenes may partly prevent the physical property studies of these compounds. Thus, it would be of interest to develop new approaches for the preparation of bismetallabenzenes and investigate their electrochemical properties.

Isocyanides have been well known to stabilize complexes by participating as not only strong σ-donors but also π-acceptor ligands.[12,13] Especially the metal−carbon π-interactions play key roles in the stability of metal−isocyanides and electronic interactions between the metal center and isocyanide ligands. Thus transition-metal complexes of organic isocyanides are widely used in organic and organometallic synthesis,[14a−c] catalysis,[14d] optoelectronic materials,[14e−i] building blocks for organometallic polymers,[15] and molecular self-assembly[12e,16] fields. In particular, multiisocyanides have been suggested as possible “alligator clips” for molecular wires and the electronic transport between metal contacts.[15d] Therefore, the multiisocyanide-bridged metal complexes have also gained importance for their versatile structural and physicochemical properties in fields including luminescence[17,18] and electronic transmission.[19,20] For example, the diisocyanide ligands, such as 1,4-diisocyanobenzene, are capable of forming structure and electronic bridges between two metal centers, facilitating electron polarization and transfer through the metal−ligand−metal system.[12,20]

In our investigation on the reactivity of metallabenzenes, we have reported that ruthenabenzene $[Ru(CHC(PPh_3)CHC(PPh_3)CH)Cl_2(PPh_3)_2]Cl$ (**1**) can readily undergo ligand substitution reaction with ^{t}BuNC to produce stable

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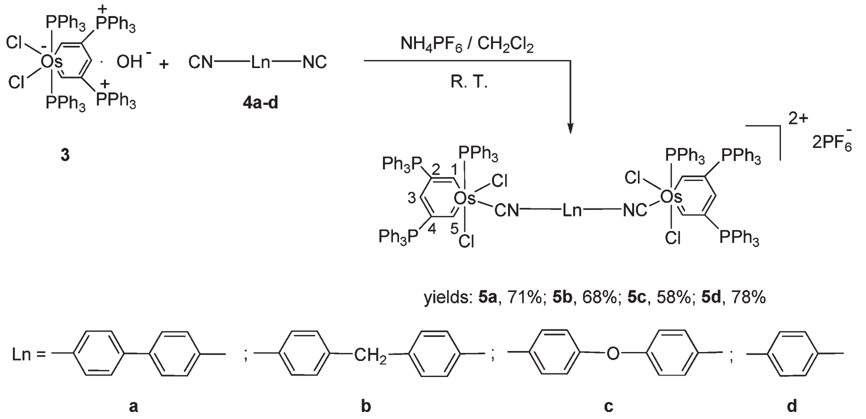
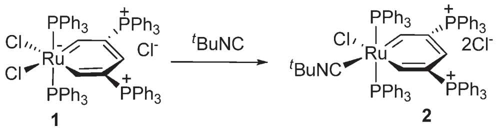
Scheme 1. Synthetic Pathways for the Bismetallabenzenes 5a−d Bridged by Diisocyanide Ligands



isocyanide-coordinated ruthenabenzene **2** (eq 1).[9] Given the important role of diisocyanides in molecular electronics and recent progress in optoelectronic materials mentioned above, we are motivated to design a new bismetallabenzene system with diisocyanide as the bridging ligands. Of particular interest is the diisocyanide-bridged bismetallabenzenes constituting large conjugated system, which might exhibit special electrochemical and other physicochemical properties.



(1)

In this work, we have successfully constructed a series of bisosmabenzenes using diisocyanides with different linking spacers as the bridging ligands. As a comparative study, a bisosmafuran bridged by 1,4-phenylenediidocyanide has also been synthesized. The electrochemical properties of several complexes have been studied by cyclic voltammetry.

Results and Discussion

Synthesis and Characterization of Diisocyanide-Bridged Bisosmabenzenes from Ligand Subtitution Reactions. As already stated, in our studies on the reactivity of ruthenabenzenes with the isocyanides,[9] we have found that one of the Cl ligands in **1** can be readily replaced by ^{t}BuNC to produce stable isocyanide-coordinated ruthenabenzene **2** (eq 1). We envisioned that analogous osmambenzene complex [Os(CHC(PPh$_3$)CHC(PPh$_3$)CH)Cl$_2$(PPh$_3$)$_2$]OH (**3**)[21] may also undergo similar ligand substitution reaction with diisocyanide. Thus, we have carried out the reaction of **3** with a series of diisocyanide ligands, with the hope to obtain bismetallabenzene complexes. As expected, a number of bisosmabenzenes have been successfully synthesized and fully characterized. The general synthetic route for the preparation of bismetallabenzenes is outlined in Scheme 1.

Treatment of osmabenzene [Os(CHC(PPh$_3$)CHC(PPh$_3$)-CH)Cl$_2$(PPh$_3$)$_2$]OH (**3**) with 0.5 equiv of diisocyanide ligand CN−Ln−NC (**4a−d**, Ln is the linking spacer) in the presence of NH$_4$PF$_6$ at room temperature for 0.5−1.0 h led to the formation of bisosmabenzenes **5a−d**, which were isolated as greenish solids in yields ranging from 58% to 78%. It was found that the reaction proceeded very slowly in the absence of NH$_4$PF$_6$, while addition of NH$_4$PF$_6$ could speed up the reaction. Probably NH$_4$PF$_6$ was added to abstract one chloride ligand first, so that the ligand substitution reaction can be accelerated. In the solid state and under an inert atmosphere, these complexes are all stable at room temperature for at least one month and can be stored at 0 °C for at least several months without appreciable decomposition. However, it is important to note that complexes **5a−d** can slowly decompose in solution at ambient temperature, resulting in the formation of a mixture of unidentified products.

All of the compounds have been characterized by elemental analysis, IR, and ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectrometry. Although the molecular structures of **5a−d** have not been characterized so far by X-ray diffraction, due to the lack of X-ray quality single crystals, it is believed that each molecule has two symmetrically related units, as inferred from the NMR data. Selected NMR and IR data for the bisosmabenzenes **5a−d** are given in Table 1. On the whole, the NMR data of **5a−d** are similar to each other with respect to chemical shifts and signal patterns. In the ^{31}P{^{1}H} NMR spectrum, each of the osmium complexes **5a−d** shows one singlet in the region δ = −1.20 to −1.83 attributed to Os*P*Ph$_3$ and another two singlets for C*P*Ph$_3$ in the regions δ = 19.74−20.65 and 24.88−25.58 ppm, respectively. In the ^{1}H NMR spectrum the characteristic signals for OsC*H* of the metallacycle are observed at δ = 14.54−15.74 ppm with a H−P coupling constant of approximately 25 Hz and δ = 16.36−17.45 ppm with a H−P coupling constant of approximately 19 Hz. The proton resonances on the carbons *para* to the Os centers appear at δ = 7.95−9.09 ppm according to ^{1}H−^{13}C HSQC. In comparison to **3**, the ^{1}H NMR signals of the ring protons for **5a−d** are shifted considerably upfielded.[5n,21] A similar trend was observed for the *meta*-carbons in the ^{13}C NMR spectrum, in which the signals of γ-*C*H are observed in the range δ = 152.76−158.91 ppm, whereas the signals of *ortho*- and *para*-carbons to the Os centers are shifted downfield, which appear in the ranges δ = 238.03−259.75 and 114.32−120.41 ppm. Additionally, the isocyano-carbon signals are generally of low intensity,[22] which appear as a singlet at δ = 143.15−145.15 ppm. In particular, only one ν(C≡N) absorption is observed for each complex at 2081−2109 cm^{-1} in the FTIR spectra, indicating the presence of one type of isocyano group in each complex.

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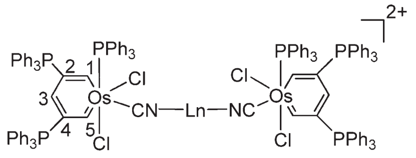
[21] Xia, H.; He, G.; Zhang, H.; Wen, T. B.; Sung, H. H. Y.; Williams, I. D.; Jia, G. *J. Am. Chem. Soc.* **2004**, *126*, 6862.

[22] Efraty, A.; Feinstein, I.; Wackerle, L.; Goldman, A. *J. Org. Chem.* **1980**, *45*, 4059.

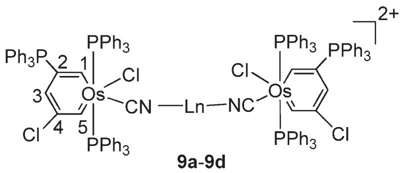
Table 1. Selected ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR and IR Data for Complexes **5a–d** and **9a–d**

	$^{31}P\{^1H\}$ (ppm)	^1H (ppm)			$^{13}C\{^1H\}$ (ppm)						IR (cm^{-1})
compd		H1	H3	H5	C1	C2	C3	C4	C5	N≡*C*	N≡C
5a	20.64, 25.58, −1.48	15.69	9.09	17.40	254.70	114.40	153.74	115.36	240.35	143.15	2095
5b	19.74, 24.88, −1.20	15.74	8.33	17.45	253.76	115.46	152.76	116.86	238.03	143.34	2109
5c	20.59, 25.48, −1.83	14.62	7.98	16.36	259.75	119.72	158.91	120.41	245.35	145.15	2081
5d	20.65, 25.36, −1.47	14.54	7.95	16.45	253.67	114.32	152.89	116.11	240.12	144.06	2088
9a	18.68, −3.34	13.73	7.79	16.62	233.40	115.48	139.47	136.53	251.94	153.18	2084
9b	18.57, −3.01	13.77	7.82	16.68	232.45	115.36	139.69	136.38	265.09	141.78	2086
9c	17.00, −5.18	13.67	7.56	16.62	233.16	115.35	139.28	136.42	251.70	156.22	2075
9d	18.67, −2.12	13.63	7.83	16.52	233.01	116.04	139.58	136.34	251.89	156.21	2064

[a] Numbering schemes for the hydrogen and carbon atoms in **5a**,**b** and **9a**,**b** are

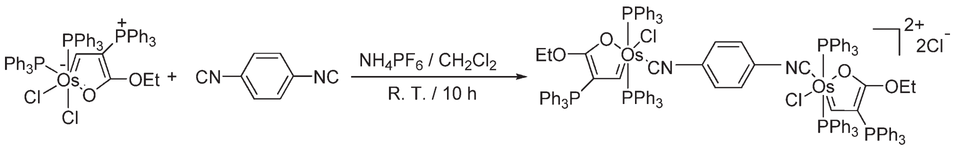


5a-5d



9a-9d

Scheme 2. Synthetic Pathways for the Bisosmafuran 7 Bridged by the 1,4-Phenylenediisocyanide Ligand



6 **4d** **7** yield: 78%

Synthesis and Characterization of 1,4-Phenylenediisocyanide-Bridged Bisosmafuran. Metallafurans, a class of five-membered metallacycles, are also a common representative of metalla-heteroaromatic compounds. As a comparative study, we have also prepared a diisocynide-bridged bisosmafuran via ligand substitution reaction. In a manner similar to that for **5a–d**, treatment at room temperature of osmafuran $[Os(CHC(PPh_3)C(OEt)O)Cl_2(PPh_3)_2]$ (**6**)[23] with 0.5 equiv of 1,4-phenylenediisocyanide in the presence of NH_4PF_6 over 10 h resulted in the formation of 1,4-phenylenediisocyanide-bridged bisosmafuran complex **7**, which was isolated as a light yellow solid after column chromatography in 78% yield (Scheme 2). Although stable in the solid state, a solution of complex **7** in CH_2Cl_2 can also slowly decompose at room temperature under an inert atmosphere.

Complex **7** has been characterized by ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR. The spectroscopic data are consistent with our proposed structural formulation. As inferred from the NMR data, it also contains two symmetrically related units. The $^{31}P\{^1H\}$ NMR spectrum shows the C*P*Ph_3 signal at δ = 14.83 ppm and the Os*P*Ph_3 signal at δ = 10.23 ppm, respectively, indicating the *trans* disposition of the two phosphine ligands. The ^1H NMR spectrum shows the characteristic OsC*H* signal as a doublet at δ = 12.73 ppm with a H−P coupling constant of 12.4 Hz. Again, in comparison to that in **5**, complex **7** displays an appreciably upfield shift in resonances for the *ortho*-protons to Os on the osmafuran rings, consistent with increased π-back-bonding between the metals and the isocyano groups in **6**. In the $^{13}C\{^1H\}$ NMR spectrum, the signals for the metallacycle carbons are observed at 239.51, 181.50, and 98.81 ppm, respectively. The signals of the ethyl groups appear at δ = 64.41 and 13.50 ppm. The ^{13}C NMR resonances of the isocyano groups appear as a singlet at δ = 145.73 ppm.

Synthesis and Characterization of Diisocyanide-Bridged Bisosmabenzenes from Nucleophilic Addition Reactions. In our previous study on the reaction of $OsCl_2(PPh_3)_3$ with terminal alkyne HC≡CCH(OH)C≡CH, which resulted in the formation of the osmabenzene $[Os(CHC(PPh_3)CHC(PPh_3)CH)Cl_2(PPh_3)_2]OH$ (**3**), we have succeeded in isolating a key intermediate, the osmacycle-containing coordinated alkyne alcohol $[Os(CH{=}C(PPh_3)CH(OH)\text{-}\eta^2\text{-}C{\equiv}CH)Cl_2(PPh_3)_2]$ (**8**).[5n,21] It has been found that the isolated complex **8** can not only readily react with PPh_3 to produce the diphosphonium osmabenzene **3** but also react with other nucleophiles such as I^- and SCN^- to give monophosphonium-substituted iodo- as well as thiocyanato-osmabenzenes via nucleophilic attack at the coordinated alkyne.[5n] Therefore, we were prompted to attempt construction of bisosmabenzenes directly from the reactions of **8** with diisocyanides in the presence of nucleophile. With this strategy, as shown in Scheme 3, bisosmabenzenes **9a–d** could be produced from the reactions of **8** with a solution of diisocyanide ligands **4a–d** in the presence of NH_4PF_6 and NaCl. After column chromatography, **9a–d** were isolated as greenish solids in modest yields ranging from 47% to 67%. Again, NH_4PF_6 was added to abstract one of the chloride ligands in **8** to accelerate the reaction, while the added NaCl can provide sufficient nucleophiles in the reaction media, which can improve the yields. Addition of excess isocyanide ligand led to the formation of unidentified insoluble product, probably some polymeric species. It should be noted that complexes **9a–d** show excellent thermal stability under N_2 atmosphere in solid state, in view of the fact that the solid sample remains almost unchanged when heated at 120 °C under an inert atmosphere over 10 h. Unlike bisosmabenzenes **5a–d**, these complexes are stable in CH_2Cl_2 solution

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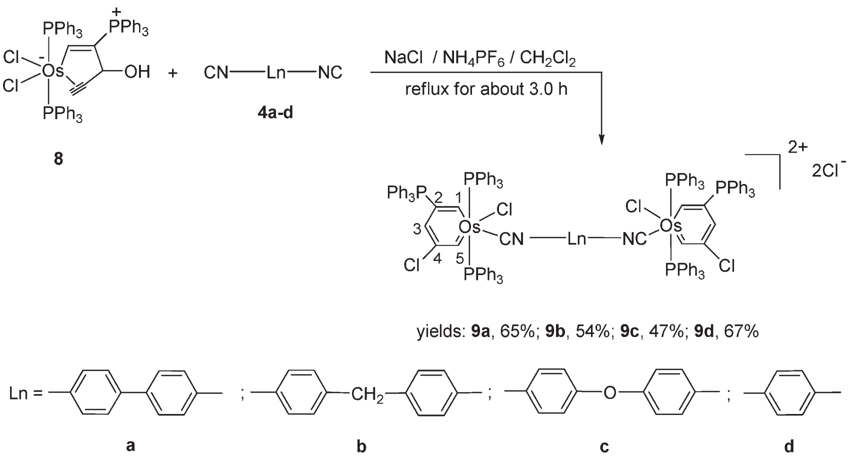
(23) Lin, Y.; Gong, L.; Xu, H.; He, X.; Wen, T. B.; Xia, H. *Organometallics* **2009**, *28*, 1524.

Scheme 3. Synthetic Pathways for the Bisosmabenzenes 9a−d Bridged by Diisocyanide Ligands



even under reflux overnight and can be stored at room temperature for at least a month without decomposition in an inert atmosphere.

Complexes **9a−d** have also been characterized by elemental analysis, IR, and multinuclear NMR spectroscopy. All data are found to be consistent with expectations. Selected NMR and IR data are shown in Table 1.

As shown in Table 1, **9a−d** exhibit NMR signals with similar chemical shifts and coupling constants, which is consistent with their nearly identical ligand environments around the Os metal centers. The ^{31}P{^{1}H} NMR spectra show two singlets in the ranges δ = 17.00−18.68 ppm (C*P*Ph$_3$) and −2.12 to −5.18 ppm (Os*P*Ph$_3$), respectively. In the ^{1}H NMR spectrum, each of the complexes **9a−d** shows a singlet in the range δ = 16.52−16.68 ppm and a doublet at δ = 13.63−13.77 ppm with a H−P coupling constant of approximately 29.0 Hz for OsC*H*CCl and OsC*H*CPPh$_3$, respectively. The *para*-protons to the metal centers on the ring give a doublet at δ = 7.56−7.83 ppm with a H−P coupling constant of approximately 13.3 Hz. The protons on the rings opposite the phosphonium groups are more downfield compared with those at the *ortho*-position in the complexes **9a−d**. This effect was also observed for our previously reported metallabenzenes with one phosphonium group on the carbon atom of the metallacycles.[5k,l,n,21] The ^{13}C NMR spectra demonstrate similar trends, that the signals for carbon atoms on the osmabenzene rings resonate in the range δ = 232.45−233.40 (Os*C*HCPPh$_3$), 251.70−265.09 (Os*C*HCCl), 136.34−136.42 (*C*Cl), 115.35−116.04 (*C*PPh$_3$), and 139.28−139.58 (CCl*C*H) ppm, respectively. Overall, complexes **9a−d** display a considerably upfield shift in resonances in comparison to **5a**,**b** due to the presence of only one phosphonium group on the metallacycle, which decreases the electronic effect.

In addition, the isocyano-carbon signals appear in the range δ = 141.78−156.22 ppm. The FTIR spectra of **9a−d** exhibit a strong IR absorption in the range ν = 2064−2086 cm^{-1} for the C≡N triple bond, which undergoes an about 30 cm^{-1} shift to lower frequency compared with those of the free ligands probably due to the M−C π-bonding interaction.[20b,24]

Repeated efforts to grow crystals of **5a−d** and **7** were unsuccessful. However, we did obtain good-quality crystals for **9d**. The structure of complex **9d** has been unambiguously established by single-crystal X-ray diffraction. A preliminary thermal ellipsoid drawing of the dication is shown in Figure 1. It confirms that complex **9d** indeed contains two six-membered metallacycles connected by a 1,4-phenylenediisocyanide bridge. This molecule is centrosymmetric, and thus the asymmetrical unit of this structure contains half a molecule. Each metallacycle contains a phosphonium and a chloro substituent at C2 and C4, respectively. The metallabenzene ring consisting of Os1/C1/C2/C3/C4/C5 is almost coplanar, which is reflected by the deviation (0.0471 Å) from the rms planes of the best fit, and the metallacycle is almost perpendicular to the benzene ring of 1,4-phenylenediisocyanide with the dihedral angle between the metallabenzene ring and the bridging benzene ring of 98.1°. The bond distances for Os1−C1 (2.046(5) Å), C1−C2 (1.383(7) Å), C2−C3 (1.424(7) Å), C3−C4 (1.366(7) Å), C4−C5 (1.401(8) Å), and Os1−C5 (1.952(5) Å), together with those for Os1−P1 (2.4013(12) Å) and Os1−Cl1 (2.5048(13) Å), are consistent with those of our previously reported osmabenzenes derivatives.[5n] As expected, the Os1−C01 (1.979(5) Å) bond is shorter than typical Os−C single bonds, whereas C01≡N1 (1.159(6) Å) is longer than the free C≡N triple bond, showing substantial π-back-bonding contribution from the metal center to the isocyanide ligand.[19a,25] The Os−C≡N bond angle of 168.7° is close to linearity. The solid-state structure of **9d** is consistent with its spectroscopic data summarized in Table 1. As mentioned above, the ^{31}P{^{1}H} NMR spectrum shows the C*P*Ph$_3$ signal at δ = 18.67 ppm and the Os*P*Ph$_3$ signal at δ = −2.12 ppm, respectively. The ^{1}H NMR spectrum shows a singlet at δ = 16.52 ppm for the OsC*H*CCl and a doublet at δ = 13.63 ppm for the OsC*H*C(PPh$_3$), whereas in the ^{13}C{^{1}H} NMR spectrum the metallacycle carbon signals are observed at 233.01 (C1), 116.04 (C2), 139.58 (C3), 136.34 (C4), and 251.89 (C5) ppm, respectively. Additionally, the C≡N stretch for the bismetallabenzene **9d** occurs at ν = 2064 cm^{-1}, somewhat lower in energy than that of the free 1,4-phenylene diisocyanide ligand (ν = 2118 cm^{-1}).[24]

Mechanistically, formation of the diisocyanide-bridged osmabenzenes **9a−d** from the reactions shown in Scheme 3 is similar to the formation of the monophosphonium-substituted iodo- as well as thiocyanato- osmabenzenes, which

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(24) Swanson, S. A.; McClain, R.; Lovejoy, K. S.; Alamdari, N. B.; Hamilton, J. S.; Scott, J. C. *Langmuir* **2005**, *21*, 5034.

(25) (a) Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Organometallics* **1998**, *17*, 4869. (b) Clark, G. R.; Waters, J. M.; Whittle, K. R. *J. Chem. Soc., Dalton Trans.* **1976**, 2029. (c) Johnson, T. W.; Tetrick, S. M.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1991**, *30*, 4146. (d) Cheung, W.-M.; Zhang, Q.-F.; William, I. D.; Leung, W.-H. *Inorg. Chem.* **2007**, *46*, 5754.

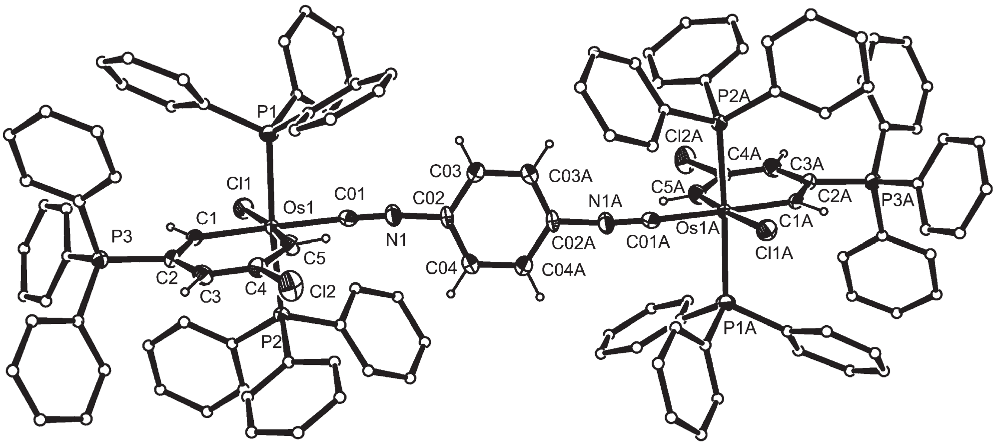
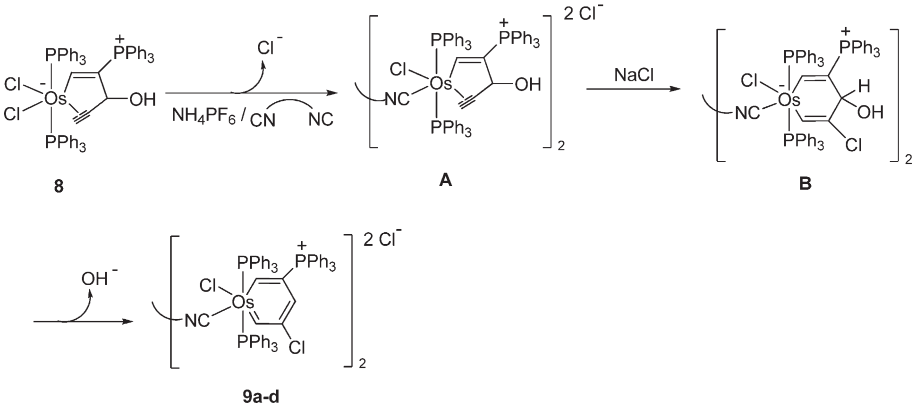


Figure 1. X-ray structure for the cation of the complex **9d** (ellipsoids at the 50% probability level). Counteranion and some of the hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms: $-x-1$, $-y+2$, $-z+1$. Selected bond distances [Å] and angles [deg]: Os(1)−C(1) = 2.046(5), C(1)−C(2) = 1.383(7), C(2)−C(3) = 1.424(7), C(3)−C(4) = 1.366(7), C(4)−C(5) = 1.401(8), Os(1)−C(5) = 1.952(5), Os(1)−C(01) = 1.979(5), Os(1)−P(1) = 2.3927(13), Os(1)−P(2) = 2.4013(12), Os(1)−Cl(1) = 2.5048(13), C(2)−P(3) = 1.800(5), C(4)−Cl(2) = 1.763(5), C(01)−N(1) = 1.159(6), C(02)−C(03) = 1.373(7), C(02)−C(04) = 1.380(7), C(02)−N(1) = 1.386(6); C(1)−Os(1)−C(5) = 87.3(2), C(1)−C(2)−C(3) = 123.6(4), C(2)−C(3)−C(4) = 122.6(5), C(3)−C(4)−C(5) = 126.7(5), C(4)−C(5)−Os(1) = 129.4(4), P(1)−Os(1)−P(2) = 168.00(4), Cl(1)−Os(1)−C(01) = 99.11(15), N(1)−C(01)−Os(1) = 168.7(5), C(01)−N(1)−C(02) = 172.5(5).

Scheme 4. Plausible Mechanism for the Formation of 9a−d



we reported previously.[5n,21] As described in Scheme 4, complex **8** can initially react with diisocyanide in the presence of NH_4PF_6 to give the diisocyanide-bridged intermediate **A**, which undergoes nucleophilic attack of the Cl^- at the coordinated alkyne, followed by elimination of an OH^- from the γ-carbon atom to give complexes **9a−d**. In fact, in our previous investigation on the related reaction of complex **8** with NaCl, we could also detect the formation of monophosphonium-substituted chloro-osmabenzene, yet the reaction is not clean, and our attempt to obtain pure sample from the crude products failed probably due to the relatively weak nucleophilicity of chloride ion and the ready decomposition of complex **8** and the formed chloro-osmabenzene in solution.[5n] It is well known that isocyanide is a good π-acidic ligand; thus replacement of a chloride ligand in **8** will decrease the electron density of the metal center and the coordinated alkyne, which facilitates the nucleophilic attack at the coordinated alkyne by the chloride ion.

Electrochemical Studies. While many theoretical studies and various synthetic methods of metallabenzenes have been reported, the electrochemical studies of metallabenzenes are still rather limited. To the best of our knowledge, our recent studies on the electrochemical properties of a series of ruthenabenzenes and osmabenzenes and their analogues are the only reported examples.[5n,9,10] Of particular interest is the electronic communication between the two metal centers observed in the trichloro-bridged bisruthenabenzenes[9] and bisosmanaphalenes.[10]

On the basis of our facile preparation strategy of the diisocyanide-bridged bismetallabenzenes mentioned above, we also intended to study their electrochemical properties. However, complexes **5a−d** and **7** could slowly decompose in solution to give a mixture of undentified products. We thus have investigated the redox behaviors of the stable bismetallabenzenes **9a−d** (1 mM in CH_2Cl_2) by cyclic voltammetry (CV) and differential pulse voltammogram techniques (DPV) with 0.1 M n-Bu_4NClO_4 as the supporting electrolyte. The values of the potentials for these complexes are presented in Table 2, and typical CVs of complexes **9a−d** are displayed in Figures 2−5.

As shown in Figures 2 and 3, the CV and DPV of complex **9a** exhibit one quasi-reversible oxidation wave at $E_{p,a}$ = +1.22 V presumably attributed to the oxidation of the osmium center. This result indicates that there is little if

Table 2. Cyclic Voltammetry Data for Complexes 9a–d in CH_2Cl_2 Containing 0.1 M n-Bu_4NClO_4[a]

	potential data/V					
	$E_{p,a,1}$	$E_{p,c,1}$	$\Delta E_{p,1}$	$E_{p,a,2}$	$E_{p,c,2}$	$\Delta E_{p,2}$
9a				1.22	1.07	0.15
9b				1.22	1.08	0.14
9c	0.58	0.38	0.20	0.77	0.59	0.19
9d	0.16	0.01	0.15	0.81	0.65	0.16

[a] Potential versus Ag/AgCl, scan rate = 0.10 V s^{-1}.

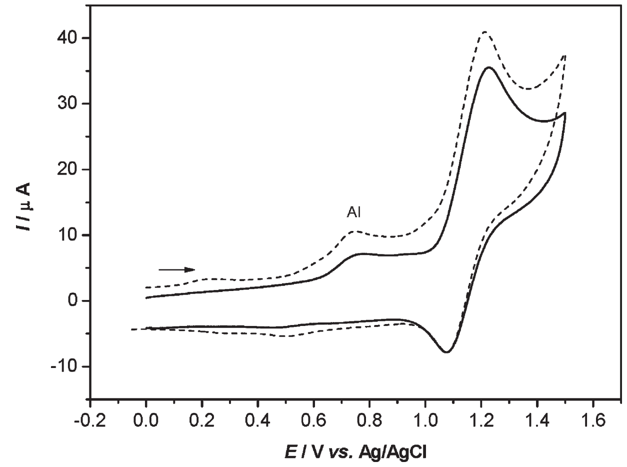


Figure 2. Cyclic voltammogram of complexes **9a** (solid line) and **9b** (dashed line) measured in CH_2Cl_2 with 0.1 M n-Bu_4NClO_4 as supporting electrolyte at a scan rate of 0.10 V s^{-1}.

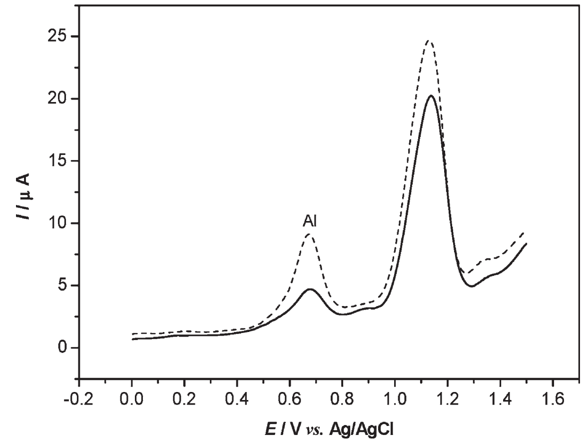


Figure 3. Differential pulse voltammograms of complexes **9a** (solid line) and **9b** (dashed line) in CH_2Cl_2 with 0.1 M n-Bu_4NClO_4 at a scan rate of 0.10 V s^{-1}.

any electronic interaction between the metal centers in complex **9a**. It is likely ascribed to rotation of two conjoining benzene rings in complex **9a**, which breaks the π-conjugated electronic communication.[26] Additionally, an adsorption prewave (AI) can be seen in the CV of complex **9a**, indicating that reactant **9a** can be strongly adsorbed on the glassy carbon electrode.[27] Similar adsorption peaks for the oxidation of **9b** can be also observed in Figures 2 and 3. The redox performance of **9b** is similar to that of **9a**. Again, no electronic interaction between the two osmium centers for complex **9b** was observed, which might be due to the lack of conjugation in **9b**.

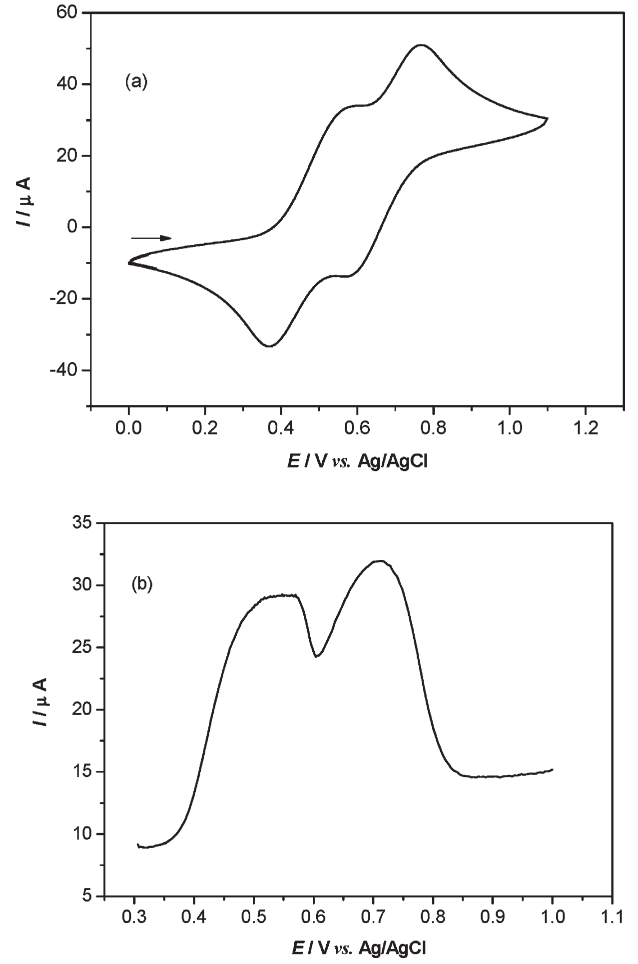


Figure 4. Cyclic (a) and differential pulse (b) voltammograms of complex **9c** in CH_2Cl_2 with 0.1 M n-Bu_4NClO_4 at a scan rate of 0.10 V s^{-1}.

Interestingly, for complex **9c**, with an oxygen atom inserted between two 1,4-phenylene groups of complex **9a**, a weak but appreciable electronic interaction between the metal centers can be observed (Figure 4). The two oxidation waves at $E_{p,a} = +0.58$ V and $E_{p,a} = +0.77$ V are partly overlapped and the ΔE for complex **9c** is found to be 0.19 V, indicating the presence of a stronger interaction between the two metal centers in **9c** than that in **9a**. Undoubtedly, an important contributor is the presence of a lone pair of electrons on the oxygen atom,[28] which provides a relatively soft set of delocalized forms through which the increase in the positive charge upon oxidation may be felt by one Os unit from the other, therefore giving rise to a considerable increase in internuclear communication between the two Os units.

As expected, a moderate metal–metal interaction is clearly observed in bismetallabenzene **9d** through the 1,4-phenylenediisocyanide bridge. As shown in Figure 5, **9d** undergoes two consecutive, chemically and electrochemically, one-electron

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(26) (a) Ghazala, S. I.; Paul, F.; Toupet, L.; Roisnel, T.; Hapiot, P.; Lapinte, C. *J. Am. Chem. Soc.* **2006**, *128*, 2463. (b) Xia, J.-L.; Wu, X.; Lu, Y.; Chen, G.; Jin, S.; Yu, G.; Liu, S. H. *Organometallics* **2009**, *28*, 2701.

(27) Wopschall, R. H.; Shain, I. *Anal. Chem.* **1967**, *39*, 1514.

(28) Rigaut, S.; Olivier, C.; Costuas, K.; Choua, S.; Fadhel, O.; Massue, J.; Turek, P.; Saillard, J.-Y.; Dixneuf, P. H.; Touchard, D. *J. Am. Chem. Soc.* **2006**, *128*, 5859.

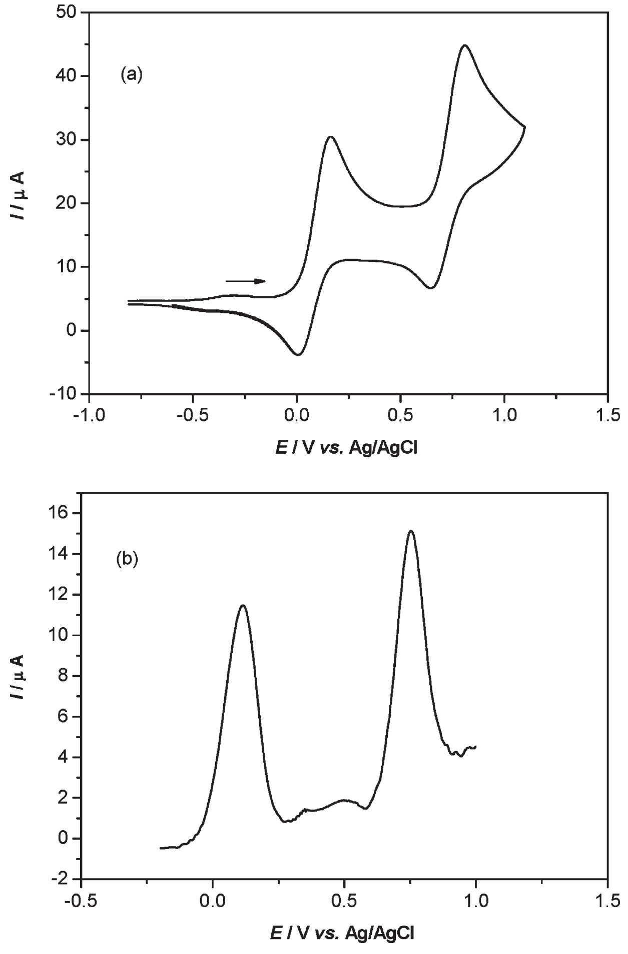

Figure 5. Cyclic (a) and differential pulse (b) voltammograms of complex **9d** in CH_2Cl_2 with 0.1 M n-Bu_4NClO_4 at a scan rate of 0.10 V s^{-1}.

oxidation processes, giving rise to redox waves at $E_{p,a}$ = +0.16 V and $E_{p,a}$ = +0.81 V, respectively. The large separation of the process (ΔE = 0.65 V) for **9d** establishes that the oxidized species are stable in solution and should correspond to the formation of [μ-(1,4-phenylenediisocyanide){Os(CHC(PPh_3)CHCClCH)Cl(PPh_3)$_2$}$_2$]$^{3+}$ and [μ-(1,4-phenylenediisocyanide){Os(CHC(PPh_3)CHCClCH)Cl(PPh_3)$_2$}$_2$]$^{4+}$, respectively.[5n] In this context, it is worthy to note that the communications between the aromatic osmabenzene ring systems in **9d** may be precluded due to the perpendicular orientation between the bridging phenyl ring and the osmabezene rings, which has already been confirmed by X-ray crystallographic study.

Conclusion

Though there have been many metallabenzene complexes synthesized so far, bismetallabenzenes and their analogues are rare and the studies of their physical properties are still rather limited. In this work, we have successfully constructed a series of diisocyanide-bridged bisosmabenzenes either via ligand substitution reactions of osmabenzenes [Os(CHC(PPh_3)CHC(PPh_3)CH)Cl_2(PPh_3)$_2$]OH with various diisocyanides or through similar ligand substitution reactions of the osmacycle [Os (CH=C(PPh_3)CH(OH)-η^2-C≡CH)Cl_2(PPh_3)$_2$] followed by nucleophilic attack at the coordinated alkyne. Electrochemical studies have shown that bisosmabenzenes [(μ-CN-R-NC){Os(CHC(PPh_3)CHCClCH)Cl(PPh_3)$_2$}$_2$]Cl_2 (**9c** R = 4,4′-oxybisphenyl; **9d** R = 1,4-phenylene) exhibit metal−metal interaction through the conjugated diisocyanide bridge and undergo two consecutive, chemically and electrochemically, one-electron redox processes.

Experimental Section

General Considerations. All manipulations were carried out at room temperature under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (diethyl ether, tetrahydrofuran) or calcium hydride (dichloromethane). The starting materials [Os(CHC(PPh_3)CHC(PPh_3)CH)Cl_2(PPh_3)$_2$]OH (**3**),[5n,21] [Os(CHC(PPh_3)C(OEt)O)Cl_2(PPh_3)$_2$] (**6**),[23] [Os(CH=C(PPh_3)-CH(OH)-η^2-C≡CH)Cl_2(PPh_3)$_2$] (**8**),[5n,21] 4,4′-biphenyldiisocyanide (**4a**),[23,29] 4,4′-diisocyanodiphenylmethane (**4b**),[30] bis(4-isocyanophenyl) ether (**4c**),[31] and 1,4-phenylenediisocyanide (**4d**)[22,32] were synthesized by literature procedures. 4,4′-Biphenylamine, 4,4′-diaminobiphenylmethane, and 4,4′-diaminobiphenyl ether were purchased from Sigma-Aldrich and Alfa Aesar. Column chromatography was performed on neutral alumina (200−300 mesh). All the NMR spectra were recorded with a Bruker AV300 (^1H 300.1 MHz; ^{13}C 75.5 MHz; ^{31}P 121.5 MHz) or a Bruker AV400 (^1H 400.1 MHz; ^{13}C 100.6 MHz; ^{31}P 162.0 MHz) spectrometer. ^1H and ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4. Elemental analyses data were obtained on a Thermo Quest Italia SPA EA 1110 instrument. Samples for infrared spectroscopy were prepared as pellets (KBr), with spectra acquired on Nicolet Avatar 370 spectrometers, Thermo Electron Corporation, U.S.A.

Cyclic voltammetry was performed at room temperature (25 °C) under N_2 atmosphere in freshly distilled CH_2Cl_2 containing 0.1 M Bu_4NClO_4 (TBAP), using a CHI660 A voltammetric analyzer. A three-electrode system in a single-compartment cell with resistance compensation was used throughout. The working electrode was a glassy carbon disk (diameter = 3 mm). This electrode was carefully polished with 1 mm, 0.3 mm, and 0.05 mm alumina powder and ultrasonically rinsed with distilled water and ethanol before each run. The auxiliary electrode was a platinum sheet, and the reference electrode was Ag/AgCl in CH_2Cl_2 with 0.1 M TBAP. The ferrocene/ferrocenium redox couple was located at 0.39 V under our experimental conditions.

CAUTION! *The aminobiphenyls are very carcinogenic materials and must be handled with extreme care. Additionally, all isocyanide preparations should be conducted in a fume hood owing to the toxic gas.*

[μ-(4,4′-Biphenyldiisocyanide){Os(CHC(PPh_3)CHC(PPh_3)-CH)Cl_2(PPh_3)}$_2$][PF_6]$_2$ (5a). To a solution of complex **3** (0.32 g, 0.23 mmol) in dry dichloromethane (30 mL) were added 4,4′-biphenyldiisocyanide (**4a**) (23 mg, 0.12 mmol) and NH_4PF_6 (38 mg, 0.23 mmol). The solution was stirred for 0.5 h at room temperature. After filtration, the solution was concentrated to ca. 5 mL. Diethyl ether was added slowly to give a green precipitate, which was collected by filtration. Recrystallization of the crude product from dichloromethane/diethyl ether gave **5a** as a deep green solid. Yield: 0.18 g, 71%. ^1H NMR ((CD_3)$_2$-CO, 300.1 MHz): δ (ppm) 17.40 (d, ^3J(PH) = 18.6 Hz, 2 H, OsCH), 15.69 (d, ^3J(PH) = 25.2 Hz, 2 H, OsCH), 9.09 (t, ^3J(PH) = 12.7 Hz, 2 H, OsCHC(PPh_3)CH), 6.54−8.12 (m, 98 H, PPh_3

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and phenylene). ^{31}P{^{1}H} NMR ((CD$_3$)$_2$CO, 121.5 MHz): δ (ppm) 25.58 (s, C*P*Ph$_3$), 20.64 (s, C*P*Ph$_3$), −1.48 (s, Os*P*Ph$_3$), −144.78 (septet, *P*F$_6$). ^{13}C{^{1}H} NMR ((CD$_3$)$_2$CO, 75.5 MHz): δ (ppm) 254.70 (d, ^{2}J(PC) = 15.1 Hz, Os*C*H), 240.35 (d, ^{2}J(PC) = 15.1 Hz, Os*C*H), 153.74 (t, ^{2}J(PC) = 21.9 Hz, OsCHC(PPh$_3$)*C*H), 143.15 (s, *C*≡N), 118.47−135.47 (m, PPh$_3$ and phenylene), 115.36 (d, ^{1}J(PC) = 71.9 Hz, OsCH*C*(PPh$_3$)), 114.40 (d, ^{1}J(PC) = 70.1 Hz, OsCH*C*(PPh$_3$)). IR (cm^{-1}): $\nu_{C\equiv N}$ = 2095 cm^{-1}. Anal. Calcd for C$_{132}$H$_{104}$Cl$_4$F$_{12}$N$_2$P$_8$Os$_2$: C, 58.37; H, 3.86; N, 1.03. Found: C, 58.25; H, 4.23; N, 1.13.

[μ-(4,4′-Diisocyanodiphenylmethane){Os(CHC(PPh$_3$)CHC(PPh$_3$)CH)Cl$_2$(PPh$_3$)}$_2$][PF$_6$]$_2$ (5b). By the same method as that for the preparation of **5a**, complex **5b** was obtained as a green solid from the reaction of **3** (0.31 g, 0.22 mmol) with 4,4′-diisocyanodiphenylmethane (**4b**) (24 mg, 0.11 mmol) in dichloromethane (30 mL) in the presence of NH$_4$PF$_6$ (37 mg, 0.22 mmol). Yield: 0.21 g, 68%. ^{1}H NMR (CD$_2$Cl$_2$, 300.1 MHz): δ (ppm) 17.45 (d, ^{3}J(PH) = 18.9 Hz, 2 H, OsC*H*), 15.74 (d, ^{3}J(PH) = 24.9 Hz, 2 H, OsC*H*), 8.33 (t, ^{3}J(PH) = 14.4 Hz, 2 H, OsCHC(PPh$_3$)C*H*), 6.39−7.99 (m, 98 H, PPh$_3$ and phenylene), 3.81 (s, C*H*$_2$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 121.5 MHz): δ (ppm) 24.88 (s, C*P*Ph$_3$), 19.74 (s, C*P*Ph$_3$), −1.20 (s, Os*P*Ph$_3$), −144.75 (septet, *P*F$_6$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 75.5 MHz): δ (ppm) 253.76 (d, ^{2}J(PC) = 15.2 Hz, Os*C*H), 238.03 (d, ^{2}J(PC) = 15.5 Hz, Os*C*H), 152.76 (t, ^{2}J(PC) = 21.8 Hz, OsCHC(PPh$_3$)*C*H), 143.34 (s, *C*≡N), 117.46−136.78 (m, PPh$_3$ and phenylene), 116.86 (d, ^{1}J(PC) = 75.6 Hz, OsCH*C*(PPh$_3$)), 115.46 (d, ^{1}J(PC) = 70.6 Hz, OsCH(*C*PPh$_3$)), 41.36 (s, *C*H$_2$). IR (cm^{-1}): $\nu_{C\equiv N}$ = 2109 cm^{-1}. Anal. Calcd for C$_{133}$H$_{106}$Cl$_4$F$_{12}$N$_2$P$_8$Os$_2$: C, 58.51; H, 3.91; N, 1.03. Found: C, 58.32; H, 3.61; N, 1.09.

[μ-(Bis(4-isocyanophenyl)ether){Os(CHC(PPh$_3$)CHC(PPh$_3$)CH)Cl$_2$(PPh$_3$)}$_2$][PF$_6$]$_2$ (5c). By the same method as that for the preparation of **5a**, complex **5c** was obtained as a green solid from the reaction of **3** (0.36 g, 0.26 mmol) with bis(4-isocyanophenyl) ether (**4c**) (28 mg, 0.13 mmol) in dichloromethane (35 mL) in the presence of NH$_4$PF$_6$ (44 mg, 0.27 mmol), Yield: 0.21 g, 58%. ^{1}H NMR ((CD$_3$)$_2$CO, 400.1 MHz): δ (ppm) 16.36 (d, ^{3}J(PH) = 19.6 Hz, 2 H, OsC*H*), 14.62 (d, ^{3}J(PH) = 25.2 Hz, 2 H, OsC*H*), 7.98 (t, ^{3}J(PH) = 13.2 Hz, 2 H, OsCHC(PPh$_3$)C*H*), 6.81−7.98 (m, 98 H, PPh$_3$ and phenylene). ^{31}P{^{1}H} NMR ((CD$_3$)$_2$CO, 162.0 MHz): δ (ppm) 25.48 (s, C*P*Ph$_3$), 20.59 (s, C*P*Ph$_3$), −1.83 (s, Os*P*Ph$_3$), −144.22 (septet, *P*F$_6$). ^{13}C{^{1}H} NMR ((CD$_3$)$_2$CO, 100.6 MHz): δ (ppm) 259.75 (d, ^{2}J(PC) = 15.4 Hz, Os*C*H), 245.35 (d, ^{2}J(PC) = 15.9 Hz, Os*C*H), 158.91 (t, ^{2}J(PC) = 21.9 Hz, OsCHC(PPh$_3$)*C*H), 145.15 (s, *C*≡N), 120.21−140.61 (m, PPh$_3$ and phenylene), 120.41 (d, ^{1}J(PC) = 70.9 Hz, OsCH*C*(PPh$_3$)), 119.72 (d, ^{1}J(PC) = 70.5 Hz, OsCH*C*(PPh$_3$)). IR (cm^{-1}): $\nu_{C\equiv N}$ = 2081 cm^{-1}. Anal. Calcd for C$_{132}$H$_{104}$Cl$_4$F$_{12}$N$_2$OP$_8$Os$_2$: C, 58.02; H, 3.84; N, 1.03. Found: C, 58.24; H, 4.04; N, 1.05.

[μ-(1,4-Phenylenediisocyanide){Os(CHC(PPh$_3$)CHC(PPh$_3$)CH)Cl$_2$(PPh$_3$)}$_2$][PF$_6$]$_2$ (5d). By the same method as that for the preparation of **5a**, complex **5d** was obtained as a green solid from the reaction of **3** (0.25 g, 0.18 mmol) with 1,4-phenylenediisocyanide (**4d**) (12 mg, 0.09 mmol) in dichloromethane (25 mL) in the presence of NH$_4$PF$_6$ (30 mg, 0.18 mmol). Yield: 0.18 g, 78%. ^{1}H NMR ((CD$_3$)$_2$CO, 300.1 MHz): δ (ppm) 16.45 (d, ^{3}J(PH) = 18.9 Hz, 2 H, OsC*H*), 14.54 (d, ^{3}J(PH) = 23.7 Hz, 2 H, OsC*H*), 7.95 (t, ^{3}J(PH) = 12.6 Hz, 2 H, OsCHC(PPh$_3$)C*H*), 6.14−7.82 (m, 94 H, PPh$_3$ and phenylene). ^{31}P{^{1}H} NMR ((CD$_3$)$_2$CO, 121.5 MHz): δ (ppm) 25.36 (s, C*P*Ph$_3$), 20.65 (s, C*P*Ph$_3$), −1.47 (s, Os*P*Ph$_3$), −144.56 (septet, *P*F$_6$). ^{13}C{^{1}H} NMR ((CD$_3$)$_2$CO, 75.5 MHz): δ (ppm) 253.67 (d, ^{2}J(PC) = 15.3 Hz, Os*C*H), 240.12 (d, ^{2}J(PC) = 15.4 Hz, Os*C*H), 152.89 (t, ^{2}J(PC) = 21.9 Hz, OsCHC(PPh$_3$)*C*H), 144.06 (s, *C*≡N), 118.65−135.45 (m, PPh$_3$ and phenylene), 116.11 (d, ^{1}J(PC) = 70.8 Hz, OsCH*C*(PPh$_3$)), 114.32 (d, ^{1}J(PC) = 70.8 Hz, OsCH*C*(PPh$_3$)). IR (cm^{-1}): $\nu_{C\equiv N}$ = 2088 cm^{-1}. Anal. Calcd for C$_{126}$H$_{100}$Cl$_4$F$_{12}$N$_2$P$_8$Os$_2$: C, 57.32; H, 3.82; N, 1.06. Found: C, 57.43; H, 4.16; N, 0.85.

[μ-(1,4-Phenylenediisocyanide){Os(CHC(PPh$_3$)C(OEt)O)Cl(PPh$_3$)$_2$}$_2$Cl$_2$ (7). A mixture of complex **6** (0.20 g, 0.18 mmol), 1,4-phenylenediisocyanide (**4d**) (11 mg, 0.09 mmol), and NH$_4$PF$_6$ (58 mg, 0.35 mmol) in CH$_2$Cl$_2$ (30 mL) was stirred at room temperature for 10 h to give a brown suspension. Evaporation of the solvent gave a solid, which was purified by column chromatography (neutral alumina, solvent: dichloromethane, eluent: dichloromethane/methanol, 20:0.3). The yellow band was collected, evaporated to dryness, and recrystallized from dichloromethane and diethyl ether to give a bright yellow powder of **7**. Yield: 0.17 g, 78%. ^{1}H NMR (CDCl$_3$, 400.1 MHz): δ (ppm) 12.73 (d, ^{3}J(PH)) = 12.4 Hz, 2 H, OsC*H*), 6.81−7.70 (m, 94 H, PPh$_3$ and phenylene), 3.98 (m, 4 H, OC*H*$_2$), 0.50 (t, ^{3}J(HH)) = 7.2 Hz, 6 H, OCH$_2$C*H*$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, 162.0 MHz): δ (ppm) 14.83 (s, C*P*Ph$_3$), 10.23 (s, Os*P*Ph$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 100.6 MHz): δ (ppm) 239.51 (m, Os*C*H), 181.50 (d, ^{2}J(PC) = 16.4 Hz, *C*(OCH$_2$CH$_3$)), 145.73 (s, *C*≡N), 98.81 (d, ^{1}J(PC) = 73.4 Hz, *C*PPh$_3$), 114.88−135.00 (m, PPh$_3$ and phenylene), 64.41 (s, O*C*H$_2$), 13.50 (s, OCH$_2$*C*H$_3$). Anal. Calcd for C$_{126}$H$_{106}$O$_2$N$_2$P$_6$Cl$_4$Os$_2$: C, 62.53; H, 4.41; N, 1.16. Found: C, 62.74; H, 4.66; N, 1.05.

[μ-(4,4′-Biphenyldiisocyanide){Os(CHC(PPh$_3$)CHCClCH)Cl(PPh$_3$)$_2$}$_2$]Cl$_2$ (9a). A Schlenk flask was charged with complex **8** (0.43 g, 0.38 mmol), 4,4′-biphenyldiisocyanide (**4a**) (39 mg, 0.19 mmol), NH$_4$PF$_6$ (63 mg, 0.38 mmol), NaCl (0.11 g, 1.91 mmol), and degassed CH$_2$Cl$_2$ (30 mL). The mixture was heated under reflux for 3 h and then allowed to cool before being filtered through Celite. Evaporation of the solution gave a solid, which was purified by column chromatography (neutral alumina, solvent: dichloromethane, eluent: dichloromethane/acetone, 3:1). The green band was collected, evaporated to dryness, and recrystallized from dichloromethane and diethyl ether to give a greenish powder of **9a**. Yield: 0.32 g, 65%. ^{1}H NMR (CD$_2$Cl$_2$, 300.1 MHz): δ (ppm) 16.62 (s, 2 H, OsC*H*CCl), 13.73 (d, ^{3}J(PH) = 27.9 Hz, 2 H, OsC*H*CPPh$_3$), 7.79 (d, ^{3}J(PH) = 13.1 Hz, 2 H, OsCHCClC*H*), 6.30−7.57 (m, 98 H, PPh$_3$ and phenylene). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 121.5 MHz): δ (ppm) 18.68 (s, C*P*Ph$_3$), −3.34 (s, Os*P*Ph$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 75.5 MHz): δ (ppm) 251.94 (s, Os*C*HCCl), 233.40 (br, Os*C*HCPPh$_3$), 153.18 (s, *C*≡N), 139.47 (d, ^{2}J(PC) = 22.4 Hz, OsCHCCl*C*H), 136.53 (d, ^{3}J(PC) = 15.5 Hz, OsCH*C*Cl), 126.22−135.05 (m, PPh$_3$ and phenylene), 115.48 (d, ^{1}J(PC) = 72.5 Hz, OsCH*C*(PPh$_3$)). IR (cm^{-1}): $\nu_{C\equiv N}$ = 2084 cm^{-1}. Anal. Calcd for C$_{132}$H$_{104}$Cl$_6$N$_2$P$_6$Os$_2$: C, 63.49; H, 4.20; N, 1.12. Found: C, 63.74; H, 4.26; N, 1.05.

[μ-(4,4′-Diisocyanodiphenylmethane){Os(CHC(PPh$_3$)CHCClCH)Cl(PPh$_3$)$_2$}$_2$]Cl$_2$ (9b). By the same method as that for the preparation of **9a**, complex **9b** was obtained as a green solid from the reaction of **8** (0.34 g, 0.28 mmol) with 4,4′-diisocyanodiphenylmethane (**4b**) (32 mg, 0.15 mmol) in dichloromethane (35 mL) in the presence of NaCl (87 mg, 1.49 mmol) and NH$_4$PF$_6$ (45 mg, 0.28 mmol). Yield: 0.21 g, 54%. ^{1}H NMR (CD$_2$Cl$_2$, 400.1 MHz): δ (ppm) 16.68 (s, 2 H, OsC*H*CCl), 13.77 (d, ^{3}J(PH) = 27.9 Hz, 2 H, OsC*H*CPPh$_3$), 7.82 (d, ^{3}J(PH) = 13.4 Hz, 2 H, OsCHCClC*H*), 6.38−7.59 (m, 98 H, PPh$_3$ and phenylene), 3.98 (s, C*H*$_2$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 162.0 MHz): δ (ppm) 18.57 (s, C*P*Ph$_3$), −3.01 (s, Os*P*Ph$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 100.6 MHz): δ (ppm) 265.09 (s, Os*C*HCCl), 232.45 (br, Os*C*HCPPh$_3$), 141.78 (s, *C*≡N), 139.69 (d, ^{2}J(PC) = 22.1 Hz, OsCHCCl*C*H), 136.38 (d, ^{3}J(PC) = 13.1 Hz, OsCH*C*Cl), 125.88−134.89 (m, PPh$_3$ and phenylene), 115.36 (d, ^{1}J(PC) = 72.7 Hz, OsCH*C*(PPh$_3$)), 42.12 (s, *C*H$_2$). IR (cm^{-1}): $\nu_{C\equiv N}$ = 2086 cm^{-1}. Anal. Calcd for C$_{133}$H$_{106}$Cl$_6$N$_2$P$_6$Os$_2$: C, 63.61; H, 4.25; N, 1.12. Found: C, 63.73; H, 4.72; N, 1.03.

[μ-(Bis(4-isocyanophenyl)ether){Os(CHC(PPh$_3$)CHCClCH)Cl(PPh$_3$)$_2$}$_2$]Cl$_2$ (9c). By the same method as that for the preparation of **9a**, complex **9c** was obtained as a green solid from the reaction of **8** (0.35 g, 0.31 mmol) with bis(4-isocyanophenyl)ether (**4c**) (34 mg, 0.15 mmol) in dichloromethane (35 mL) in the presence of NaCl (0.12 g, 1.98 mmol) and NH$_4$PF$_6$ (52 mg, 0.32 mmol). Yield: 0.18 g, 47%. ^{1}H NMR (CDCl$_3$, 400.1 MHz): δ (ppm) 16.62 (s, 2 H, OsC*H*CCl), 13.67 (d, ^{3}J(PH) = 30.4 Hz, 2 H, OsC*H*CPPh$_3$), 7.56 (d, ^{3}J(PH) = 13.2 Hz, 2 H, OsCHCClC*H*), 6.23−7.36 (m, 98 H, PPh$_3$ and phenylene). ^{31}P{^{1}H} NMR

Table 3. Crystal Data and Structure Refinement for 9d

	9d$\cdot 2CH_2Cl_2 \cdot 4H_2O$
empirical formula	$C_{126}H_{100}Cl_8N_2Os_2P_6 \cdot 2CH_2Cl_2 \cdot 4H_2O$
fw	2733.82
temperature, K	173(2)
radiation (Mo Kα), Å	0.71073
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	13.2136(4)
b, Å	13.7646(4)
c, Å	18.1729(6)
α, deg	103.599(3)
β, deg	99.835(3)
γ, deg	95.375(2)
V, Å^3	3134.34(17)
Z	1
d_{calcd}, g cm^{-3}	1.448
$F(000)$	1372
cryst size, mm^3	0.2 × 0.2 × 0.05
θ range, deg	2.35−25.00
reflns collected	27 768
indep reflns	10 764
obsd reflns ($I > 2\sigma(I)$)	8964
data/restraints/params	10 764/60/704
goodness-of-fit on F^2	1.000
final R ($I > 2\sigma(I)$)	R1 = 0.0368, wR2 = 0.0927
R indices (all data)	R1 = 0.0487, wR2 = 0.0955

($CDCl_3$, 162.0 MHz): δ (ppm) 17.00 (s, C*P*Ph$_3$), −5.18 (s, Os*P*Ph$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 251.70 (s, Os*C*HCCl), 233.16 (br, Os*C*HCPPh$_3$), 156.22 (s, *C*≡N), 139.28 (d, ^2J(PC) = 22.1 Hz, OsCHCCl*C*H), 136.42 (d, ^3J(PC) = 11.5 Hz, OsCH*C*Cl), 126.20−135.01 (m, PPh$_3$ and phenylene), 115.35 (d, ^1J(PC) = 72.6 Hz, OsCH*C*(PPh$_3$)). IR (cm^{-1}): $\nu_{C≡N}$ = 2075 cm^{-1}. Anal. Calcd for $C_{132}H_{104}Cl_6N_2OP_6Os_2$: C, 63.08; H, 4.17; N, 1.11. Found: C, 63.34; H, 4.38; N, 1.08.

[*μ*-(1,4-Phenylenediisocyanide){Os(CHC(PPh$_3$)CHCClCH)-Cl(PPh$_3$)$_2$}$_2$]Cl$_2$ (9d). By the same method as that for the preparation of **9a**, complex **9d** was obtained as a green solid from the reaction of **8** (0.32 g, 0.28 mmol) with 1,4-phenylenediisocyanide (**4d**) (18 mg, 0.14 mmol) in dichloromethane (30 mL) in the presence of NaCl (82 mg, 1.40 mmol) and NH_4PF_6 (45 mg, 0.28 mmol). Yield: 0.23 g, 67%. ^1H NMR (CD_2Cl_2, 300.1 MHz): δ (ppm) 16.52 (s, 2 H, OsC*H*CCl), 13.63 (d, ^3J(PH) = 28.5 Hz, 2 H, OsC*H*CPPh$_3$), 7.83 (d, ^3J(PH) = 13.6 Hz, 2 H, OsCHCClC*H*), 6.01−7.63 (m, 94 H, PPh$_3$ and phenylene). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ (ppm) 18.67 (s, C*P*Ph$_3$), −2.12 (s, Os*P*Ph$_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz): δ (ppm) 251.89 (s, Os*C*HCCl), 233.01 (br, Os*C*HCPPh$_3$), 156.21 (s, *C*≡N), 139.58 (d, ^2J(PC) = 22.7 Hz, OsCHCCl*C*H), 136.34 (d, ^3J(PC) = 12.8 Hz, OsCH*C*Cl), 126.32−135.17 (m, PPh$_3$ and phenylene), 116.04 (d, ^1J(PC) = 74.8 Hz, OsCH*C*(PPh$_3$)). IR (cm^{-1}): $\nu_{C≡N}$ = 2064 cm^{-1}. Anal. Calcd for $C_{126}H_{100}Cl_6N_2P_6Os_2$: C, 62.50; H, 4.16; N, 1.16. Found: C, 62.39; H, 4.22; N, 1.13.

X-ray Crystal Structures Determination of 9d. Data collections were performed on an Oxford Gemini S Ultra CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 173 K. Multiscan or empirical absorption corrections (SADABS) were applied. All structures were solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least-squares on F^2 using the Bruker SHELXTL-97 program package. All non-H atoms were refined anisotropically. Hydrogen atoms were introduced at their geometric positions and refined as riding atoms unless otherwise stated. CCDC-745238 (**9d**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Details on crystal data, data collection, and refinements are summarized in Table 3.

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Supporting Information Available: X-ray crystallographic files (CIF). These materials are available free of charge via the Internet at http://pubs.acs.org.