dependent on low-symmetry distortions. The second difference, i.e. the low-energy splitting between the π^*_v and π^*_σ transitions, indicates that excited-state interactions which should be different for the cobalt and the copper dimer, are important. The cobalt peroxo dimer is a closed-shell system; hence, triplet excited states should always be lower in energy than the corresponding singlets. In contrast, the copper dimer has two unpaired electrons, one on each copper center, and interactions in CT excited states can be strongly antiferromagnetic. It is interesting to note that, in agreement with this interpretation, SW–Xα calculations[30] predict a splitting between the π^*_v and π^*_σ transitions of 8500–23 000 cm^{-1} for a trans μ-1,2-peroxo copper dimer, which is much closer to the value observed for the cobalt dimer than for the copper dimer. Since the calculated value averages out excited-state exchange splittings, the difference between the theoretical and experimental values must be due to excited-state exchange interactions. In fact, large antiferromagnetic interactions have been observed in CT bands of dimers.[4c] We are now developing a general theoretical approach to describe and calculate charge-transfer excited-state dimer splittings.[31]

Acknowledgment. We thank R. Musselman and F. Fronczek for crystal structures of two systems and B. Hedman for assistance with the four-cycle diffractometer. F.T. acknowledges the Deutsche Forschungsgemeinschaft (DFG) for a postdoctoral fellowship, and E.I.S. thanks the NIH (Grant DK-31450) for support of this research.

Registry No. [NH$_3$]SCN, 18496-85-0; [NH$_3$]NO$_3$SCN, 138877-17-5; [NH$_3$-tren]SCN, 38967-82-7; [NH$_3$-tren]SO$_4$, 138856-07-2; [en-dien]-ClO$_4$, 40685-52-7.

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[30] Ross, P. K.; Solomon, E. I. *J. Am. Chem. Soc.* **1991**, *113*, 3246.

[31] Tuczek, F.; Solomon, E. I. To be published.

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(*o*-Phenylenediimido)- and (*p*-Phenylenediimido)ditungsten Complexes

Mong Liang and Eric A. Maatta*

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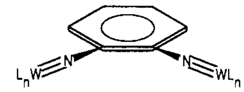
The preparations of a series of dinuclear complexes of W(VI), W(V), and W(IV), bridged by either *o*- or *p*-phenylenediimido ligands, are described. The insoluble (and presumably polymeric) d^0–d^0 systems, *o*- and *p*-[Cl$_4$W$\equiv$NC$_6$H$_4$N$\equiv$WCl$_4$], are obtained in high yield from the reactions of either *o*- or *p*-Me$_3$SiNHC$_6$H$_4$NHSiMe$_3$ with 2 equiv of WCl$_6$ in CH$_2$Cl$_2$ solution at room temperature. Upon treatment with tetrahydrofuran, these systems produce the soluble 16-electron complexes *o*- and *p*-[(THF)Cl$_4$W$\equiv$NC$_6$H$_4$N$\equiv$WCl$_4$(THF)]. It is proposed that the THF ligands occupy sites trans to the organoimido ligands in these systems. The THF ligands in the para-disubstituted complex are readily displaced by chloride ions upon treatment with [PPN]Cl to afford the decachloro dianion [PPN]$_2$[Cl$_5$W$\equiv$NC$_6$H$_4$N$\equiv$WCl$_5$]. The ortho- and para-disubstituted THF derivatives each undergo facile reduction in solution in the presence of tertiary phosphines L to produce the W(V)–W(V) (d^1–d^1) systems *o*- and *p*-[L$_2$Cl$_3$W$\equiv$NC$_6$H$_4$N$\equiv$WCl$_3$L$_2$]. ESR spectra are consistent with the adoption of the *mer*-trichloro, *trans*-bis(phosphine) geometry for these complexes. Preliminary studies of the magnetic properties of these d^1–d^1 systems throughout the temperature range 5–300 K have revealed antiferromagnetic behavior in *p*-[L$_2$Cl$_3$W$\equiv$NC$_6$H$_4$N$\equiv$WCl$_3$L$_2$] (L = Et$_2$PhP) and in *o*-[L$_2$Cl$_3$W$\equiv$NC$_6$H$_4$N$\equiv$WCl$_3$L$_2$] (L = Me$_3$P). When these W(V)–W(V) systems are treated with sodium amalgam in the presence of additional phosphine, diamagnetic W(IV)–W(IV) (d^2–d^2) systems are obtained in high yield. In the case of para-disubstituted system, the product has the stoichiometry [L$_3$Cl$_2$W$\equiv$NC$_6$H$_4$N$\equiv$WCl$_2$L$_3$] (L = Et$_2$PhP), and NMR studies suggest the adoption of the *cis*-dichloro, *mer*-tris(phosphine) geometry. In the case of the ortho-disubstituted system, the stoichiometry of the product obtained appears to depend on the steric bulk of the phosphine ligand employed. Use of the compact Me$_3$P species allows coordination of three phosphines per W atom, and the product obtained is of the form [L$_3$Cl$_2$W$\equiv$NC$_6$H$_4$N$\equiv$W$\equiv$Cl$_2$L$_3$]; a *cis*-dichloro, *mer*-tris(phosphine) geometry is again indicated by NMR studies. In the case of the bulkier Et$_2$PhP ligand, the product incorporates only two phosphines per W atom and is of the form [L$_2$Cl$_2$W$\equiv$NC$_6$H$_4$N$\equiv$WCl$_2$L$_2$]; the observed equivalence of the phosphine ligands in this species can be accommodated by a structure derived from either a square-based pyramid or a trigonal bipyramid.

Introduction

In previous papers in this series, we have described the construction of a series of dinuclear systems of molybdenum[1] and rhenium[2] bridged by *p*-phenylenediimido ligands, for which *p*-phenylenediazide, N$_3$C$_6$H$_4$N$_3$, and *p*-phenylenebis(triphenylphosphineimine), Ph$_3$P=NC$_6$H$_4$N=PPh$_3$, respectively served as the sources of the phenylenediimido unit. Subsequently, Andersen[3] reported synthetic and magnetic studies on a pair of bimetallic uranium(V) systems containing *p*- and *m*-phenylenediimido bridges; the corresponding phenylenediazide reagents served as the sources of the bridging groups in this study. We have found that trimethylsilyl derivatives of arylenediamines can also serve to introduce arylenediimido ligands into a variety of transition metal frameworks, and we now report our studies on a series of dinuclear systems of W(VI), W(V), and W(IV) containing either *o*- or *p*-phenylenediimido bridges. The resulting frameworks are depicted below.



Results

Dinuclear Tungsten(VI) Systems. The reactions of either the 1,2- or the 1,4-isomer of *N,N'*-bis(trimethylsilyl)phenylenediamine with 2 equiv of WCl$_6$ proceed readily in CH$_2$Cl$_2$ solution at room temperature to provide the dinuclear W(VI) complexes *o*- and *p*-[Cl$_4$W$\equiv$NC$_6$H$_4$N$\equiv$WCl$_4$], ***o*-1** and ***p*-1**, as shown in eq 1.[4] The

$$\text{o- or p-Me}_3\text{SiNHC}_6\text{H}_4\text{NHSiMe}_3 + 2\text{WCl}_6 \rightarrow \text{o- or p-[Cl}_4\text{W}\equiv\text{NC}_6\text{H}_4\text{N}\equiv\text{WCl}_4] \quad (1)$$

***o*-1**: ortho isomer
***p*-1**: para isomer

products are obtained as greenish-brown powders in high yields (***o*-1**, 79%; ***p*-1**, 90%), and both are virtually insoluble in nonco-

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[1] Maatta, E. A.; Devore, D. D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 569.

[2] Maatta, E. A.; Kim, C. *Inorg. Chem.* **1989**, *28*, 623.

[3] Rosen, R. K.; Andersen, R. A.; Edelstein, N. M. *J. Am. Chem. Soc.* **1990**, *112*, 4588.

[4] The corresponding reaction of *N,N'*-bis(trimethylsilyl)-1,3-phenylenediamine with WCl$_6$ likewise affords the analogous meta-disubstituted system *m*-[Cl$_4$W$\equiv$NC$_6$H$_4$N$\equiv$WCl$_4$], but we have not yet developed the chemistry of this complex: Maatta, E. A.; Jha, S. K. Unpublished results.

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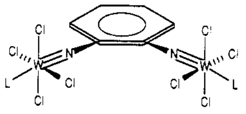
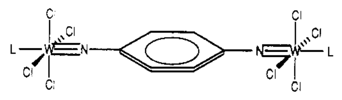
ordinating solvents. As molecular entities, complexes **1** would exhibit formal 14-electron configurations, and this fact, coupled with the observation of their insolubiity, suggests that the complexes exist as chloride-bridged systems in the solid state. When complexes **1** are treated with tetrahydrofuran, lime green THF adducts, **2**, are produced (eq 2).

$$o\text{-}\mathbf{1}/p\text{-}\mathbf{1} + \mathrm{THF} \rightarrow o\text{-}/p\text{-}[(\mathrm{THF})\mathrm{Cl_4W{\equiv}NC_6H_4N{\equiv}WCl_4(THF)}] \quad (2)$$


o-2: L = THF


p-2: L = THF

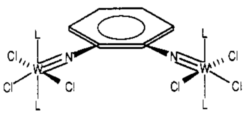
The 16-electron species **2** are appreciably soluble in common aprotic organic solvents and decompose quickly upon exposure to the atmosphere. Complexes **2** likely display structures wherein the THF ligands occupy sites trans to the imido functions; such a geometry has been established by X-ray crystallography for the related monomeric *p*-tolylimido system [TolN≡WCl$_4$(THF)].[5]

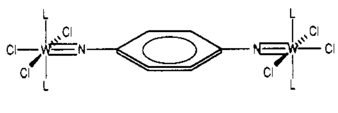
Treatment of a CH$_2$Cl$_2$ solution of *p*-**2** with 2 equiv of [PPN]Cl results in the ready replacement of the THF ligands by chloride ions, forming the decachloro dianion *p*-[Cl$_5$W≡NC$_6$H$_4$N≡WCl$_5$][PPN]$_2$, as a dark green powder in 73% yield, as shown in eq 3.[6]

$$2[\mathrm{PPN}]\mathrm{Cl} + p\text{-}\mathbf{2} \rightarrow p\text{-}[\mathrm{Cl_5W{\equiv}NC_6H_4N{\equiv}Cl_5}][\mathrm{PPN}]_2 \quad (3)$$

Dinuclear Tungsten(V) Systems. When toluene solutions containing the ditungsten complexes **2** are treated with organophosphine reagents, metal-centered reduction occurs affording the d^1–d^1 ditungsten(V) systems *o*- and *p*-[L$_2$Cl$_3$W≡NC$_6$H$_4$N≡WCl$_3$L$_2$] (**3**) as shown in eq 4. Complexes **3** are obtained as brownish powders in yields ranging from 80 to 90%. The ortho and para complexes **3** are ESR active in solution at room temperature. Their ESR spectra are all similar and consist of a principal triplet near $g = 1.90$ arising from the coupling of the unpaired electron on each W(V) center with two equivalent phosphorus nuclei; $A(^{31}\mathrm{P})$ values are approximately 30 G. These ESR data are consistent with the adoption of a *mer*-trichloro, *trans*-bis(phosphine) geometry at each tungsten site. An X-ray crystallographic study of *p*-[Cl$_3$(Me$_2$PhP)$_2$W≡NC$_6$H$_4$N≡W(PPhMe$_2$)$_2$Cl$_3$] has confirmed this geometry.[7] The ortho complex *o*-**3a** containing Me$_3$P is markedly more air-sensitive than either the ortho or para complex of Et$_2$PhP: whereas the latter two systems may be manipulated briefly as solids in the air without noticeable decomposition, the solid Me$_3$P complex decomposes quickly upon exposure to the atmosphere.

$$o\text{-}\mathbf{2}/p\text{-}\mathbf{2} + 4\mathrm{L} \rightarrow o\text{-}/p\text{-}[\mathrm{L_2Cl_3W{\equiv}NC_6H_4N{\equiv}WCl_3L_2}] \quad (4)$$

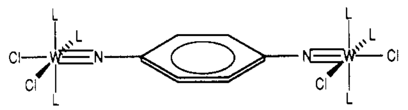

o-3a: L = Me$_3$P; o-3b: L = Et$_2$PhP


p-3: L = Et$_2$PhP

We have begun to examine the variable-temperature magnetic susceptibility of these and related d^1–d^1 systems.[8] Preliminary results have been obtained on the complexes *o*-**3a** and *p*-**3**; these data indicate antiferromagnetic behavior for both systems.

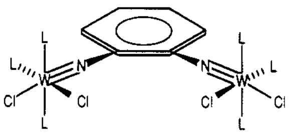
Dinuclear Tungsten(IV) Systems. Treatment of a toluene solution of *p*-**3** with excess sodium amalgam in the presence of Et$_2$PhP affords the d^2–d^2 system *p*-[L$_3$Cl$_2$W≡NC$_6$H$_4$N≡WCl$_2$L$_3$] (*p*-**4**) as shown in eq 5. The product is obtained as a golden powder in 72% yield and exhibits moderate air-stability and good solubility in common organic solvents. The complex is diamagnetic, as expected for the (d$_{xy}$)^2 configuration of each tungsten atom, and displays a characteristic singlet peak at δ 6.73 in its ^{1}H NMR spectrum arising from the equivalent phenylene ring protons. The ^{31}P{^{1}H} NMR spectrum contains two resonances at δ −2.30 and −7.86 of relative areas 1:2; although no phosphorus–phosphorus coupling was observed, each resonance displays ^{183}W satellite peaks with $J_{\mathrm{W-P}} = 378$ and 291 Hz, respectively. A variety of related monomeric d^2 tungsten and molybdenum systems of the form [RN≡MCl$_2$L$_3$] have been shown to adopt the *cis*-dichloro, *mer*-tris(phosphine) geometry.[9] Our data are consistent with the presence of this configuration at each tungsten site, but are not sufficient to distinguish between two possible structures of overall symmetry C_{2h} and C_{2v}, differentiated by the mutual disposition of the two tungsten coordination spheres.

$$p\text{-}\mathbf{3} + 2\mathrm{L} \xrightarrow{\mathrm{Na/Hg}} p\text{-}[\mathrm{L_3Cl_2W{\equiv}NC_6H_4N{\equiv}WCl_2L_3}] \quad (5)$$


p-4: L = Et$_2$PhP

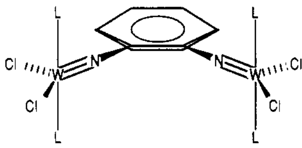
The two *o*-**3** complexes are likewise reducible to d^2–d^2 systems, but the stoichiometries of the resultant products differ, presumably reflecting the different steric demands of the Me$_3$P and Et$_2$PhP ligand sets. In the case of the *o*-**3a** complex of Me$_3$P as shown in eq 6, reduction by sodium amalgam in the presence of additional Me$_3$P proceeds in a manner analogous to that described for the *p*-**3** system above. The product, *o*-**4a**, is obtained as a yellow powder in 81% yield. ^{1}H, ^{13}C, and ^{31}P NMR spectra establish the presence of a meridional arrangement of the three Me$_3$P groups and, as described above, a *cis*-dichloro, *mer*-tris(phosphine) geometry is probable.

$$o\text{-}\mathbf{3a} + 2\mathrm{L} \xrightarrow{\mathrm{Na/Hg}} o\text{-}[\mathrm{L_3Cl_2W{\equiv}NC_6H_4N{\equiv}WCl_2L_3}] \quad (6)$$


o-4a: L = Me$_3$P

In the case of the Et$_2$PhP complex *o*-**3b**, reduction by sodium amalgam in the presence of excess added Et$_2$PhP produces a d^2–d^2 species without incorporation of additional phosphine, as shown in eq 7. The product, *o*-**4b**, is isolated as a yellow powder in 80% yield. *o*-**4b** possesses a 16-electron configuration at each tungsten atom and is slightly air-sensitive as a solid; in CDCl$_3$ solution under

$$o\text{-}\mathbf{3b} + 2\mathrm{L} \xrightarrow{\mathrm{Na/Hg}} o\text{-}[\mathrm{L_2Cl_2W{\equiv}NC_6H_4N{\equiv}WCl_2L_2}] \quad (7)$$


o-4b: L = Et$_2$PhP

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[5] Bradley, D. C.; Errington, R. J.; Hursthouse, M. B.; Short, R. L.; Ashcroft, B. R.; Clark, G. R.; Nielson, A. J.; Rickard, C. E. F. *J. Chem. Soc., Dalton Trans.* **1987**, 2067.

[6] Preliminary electrochemical studies have revealed that [Cl$_5$W≡NC$_6$H$_4$N≡WCl$_5$]$^{2-}$ undergoes two reversible one-electron reductions in THF solvent. The first such reduction corresponds to the formation of a mixed-valence W(VI)–W(V) system. Further studies are underway and will be reported separately: Geiger, W. E.; Maatta, E. A. Work in progress.

[7] Clegg, W.; Errington, R. J.; Hockless, D. C. R.; Kirk, J. M.; Redshaw, C. *Polyhedron*, in press.

[8] Liang, M.; Maatta, E. A.; McCormick, B. J.; Kahol, P. K.; Chen, S. Work in progress. A complete report on the magnetism of these and related systems will be published separately.

[9] See reference 5 and, e.g., the following: (a) Chou, C. Y.; Devore, D. D.; Huckett, S. C.; Maatta, E. A.; Huffman, J. C.; Takusagawa, F. *Polyhedron* **1986**, *5*, 301. (b) Su, F.-M.; Bryan, J. C.; Jang, S.; Mayer, J. M. *Ibid.* **1989**, *8*, 1261. (c) Lichtenhan, J. D.; Critchlow, S. C.; Doherty, N. M. *Inorg. Chem.* **1990**, *29*, 439.

N_2, immediate decomposition occurs, producing an unidentified paramagnetic material. In the ^1H NMR spectrum of the complex in C_6D_6 solution, the phenylene protons display a characteristic AA′BB′ pattern centered at δ 6.86 and 6.06; these resonances are considerably upfield of those displayed by the analogous 16-electron d^0–d^0 system, *o*-**2** (δ 7.76 and 7.45). The $^{31}P(^1H)$ NMR spectrum contains a single resonance at δ 6.28 that displays satellite coupling to ^{183}W (J_{P-W} = 412 Hz). Structures deriving from either the square-based pyramid or the trigonal bipyramid can provide the observed equivalence of the phosphine ligands in *o*-**4b**, and our spectroscopic data alone are not sufficient to provide a structural assignment.

Discussion

Trimethylsilylamines have found widespread use in the preparation of various mononuclear transition metal organoimido complexes.[10] *N,N′*-Bis(trimethylsilyl) derivatives of aromatic diamines are now likewise shown to be useful reagents for coupling transition metal fragments with an arylenediimido bridge; given the large array of diamine (and polyamine) derivatives that are readily available, this methodology is thus expected to provide convenient access to a broad range of systems containing a variety of linkages. Our preliminary results portend rich electro- and magnetochemistries for arylenediimido-bridged complexes.

The *p*-phenylenediimido-bridged ditungsten systems reported herein are analogous to the set of dimolybdenum complexes which we reported previously,[1] while the corresponding *o*-phenylenediimido ditungsten systems are apparently the first examples of complexes incorporating this ligand. Simple calculations indicate that the W–W separation in the *o*-phenylenediimido systems should be on the order of only 4.5 Å. Given this rather close approach of the tungsten centers, the congruity between the two isomeric sets of ditungsten complexes, as indicated by their identical stoichiometries, is striking. We anticipate that the geometries around the tungsten atoms in the *o*-phenylenediimido systems will display significant distortions (as compared to those of the *p*-phenylenediimido complexes) in order to alleviate intramolecular repulsions between the two tungsten coordination spheres. Unfortunately, we have yet to be able to grow crystals of an *o*-phenylenediimido complex that are suitable for an X-ray structural determination.

One key difference between the ditungsten and dimolybdenum systems is the reluctance of the former to be reduced beyond the d^2 level: while the $[W^V]_2$ systems react with sodium amalgam to give diamagnetic $[W^{IV}]_2$ products exclusively, the corresponding reaction of the $[Mo^V]_2$ complexes proceeds to yield paramagnetic, presumably $[Mo^{III}]_2$, products. The preparation of $[Mo^{IV}]_2$ systems requires the use of a milder reducing agent such as zinc amalgam, which we have found to be ineffective for the $[W^V]_2 \rightarrow [W^{IV}]_2$ conversion. These observations are in accord with general trends in the relative ease of reduction among the group VI metals.

Experimental Section

All manipulations were performed under an atmosphere of dry, purified nitrogen using glovebox, Schlenk, or vacuum line techniques. Solvents were dried using appropriate reagents, distilled, and transferred directly into reaction vessels. Bis(triphenylphosphoranylidene)ammonium chloride, [PPN]Cl, was dried under vacuum at 50 °C for 24 h before use. All other chemials were obtained from standard sources and were used as received. NMR spectra were recorded on a Bruker WM-400 instrument operating at 400.1, 100.6, and 161.9 MHz for ^1H, ^{13}C, and ^{31}P, respectively. Chemical shifts are reported in ppm relative to Me_4Si (^1H and ^{13}C) or to external 30% H_3PO_4/D_2O (^{31}P). Spectra were recorded at 23 °C except as noted. ESR spectra were recorded using a Bruker ER 200D spectrometer operating near 9.27 GHz and were calibrated using DPPH as an external field marker. Elemental analyses were performed by Galbraith Laboratories.

Preparation of Me_3SiNH-1,4-$C_6H_4NHSiMe_3$. A stirred solution of 1,4-phenylenediamine (2.0 g; 18.5 mmol) in 50 mL of THF was maintained at 0 °C while a 2.5 M n-BuLi solution in hexane (16 mL, 40 mmol) was added dropwise. The mixture was allowed to warm to room temperature and stirred for 2 h, after which time solvent was removed under vacuum and 100 mL of Et_2O was added. The resulting yellow suspension was then cooled to 0 °C and stirred vigorously while neat Me_3SiCl (4.77 g, 44 mmol) was added slowly. After the addition was complete, the mixture was stirred at 25 °C for 2 h and filtered through a Celite pad, which was subsequently eluted with an additional 60 mL of Et_2O. The volatile components of the filtrate were removed under vacuum to give the yellow-orange solid product (4.36 g; 93% yield). The material may be sublimed (50 °C; ca. 1×10^{-3} Torr) to provide light yellow crystals in good yield (77%). ^1H NMR ($CDCl_3$): δ 6.49 (s, 4 H, $C_6\mathit{H}_4$), 3.04 (s, 2 H, $N\mathit{H}$), 0.22 (s, 18 H, $Si\mathit{Me}_3$). $^{13}C(^1H)$ NMR: δ 138.49, 117.33, 0.17.

Preparation of Me_3SiNH-1,2-$C_6H_4NHSiMe_3$. A stirred solution of 1,2-phenylenediamine (2.0 g; 18.5 mmol) in 50 mL of THF was maintained at 0 °C while a 2.5 M solution of *n*-BuLi in hexane (16 mL, 40 mmol) was added dropwise. The mixture was warmed to room temperature and stirred for 3 h, after which time the solvent was removed under vacuum and 100 mL of Et_2O was added. The resulting yellow suspension was then cooled to 0 °C and stirred vigorously while neat Me_3SiCl (5.99 g, 55 mmol) was added slowly. After the addition was complete, the mixture was stirred at 25 °C for 4 h and filtered through a Celite pad, which was subsequently eluted with an additional 60 mL of Et_2O. The volatile components of the filtrate were removed under vacuum to afford the crude product as a red oil. Purification by vacuum distillation (60 °C; ca. 1×10^{-3} Torr) affords the product as a light yellow liquid (3.85 g; 82% yield). ^1H NMR ($CDCl_3$): δ 6.82–6.79 (m, 2 H, $C_6\mathit{H}_4$), 6.73–6.70 (m, 2 H, $C_6\mathit{H}_4$), 3.06 (s, 2 H, $N\mathit{H}$), 0.22 (s, 18 H, $Si\mathit{Me}_3$).

Preparation of *p*-$[Cl_4W{\equiv}NC_6H_4N{\equiv}WCl_4]$. At room temperature, a solution of Me_3SiNH-1,4-$C_6H_4NHSiMe_3$ (1.15 g; 4.56 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a stirred solution of WCl_6 (3.9 g; 9.83 mmol) in CH_2Cl_2 (50 mL). A green-brown color developed immediately and the mixture was stirred for 12 h. The dark green insoluble product was collected by filtration, washed with CH_2Cl_2 (3 × 50 mL), and dried under vacuum (3.1 g; 90% yield).

Preparation of *p*-$[(THF)Cl_4W{\equiv}NC_6H_4N{\equiv}WCl_4(THF)]$. *p*-$[Cl_4W{\equiv}NC_6H_4N{\equiv}WCl_4]$ (2.6 g, 3.4 mmol) was dissolved in a minimum amount of THF (ca. 30 mL) and stirred for 30 min. The solution was then allowed to stand undisturbed for 1 h. The lime green precipitate which formed was collected by filtration, washed with hexane (50 mL), and dried under vacuum (2.45 g; 80% yield). ^1H NMR ($CDCl_3$): δ 7.68 (s, 4 H, $C_6\mathit{H}_4$), 4.81 (t, 8 H, $\overline{\mathrm{OC}\mathit{H}_2\mathrm{CH_2CH_2C}}\mathit{H}_2$), 2.22 (quintet, 8 H, $\overline{\mathrm{OCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{C}}\mathrm{H_2}$). $^{13}C(^1H)$ NMR ($CDCl_3$): δ 130.4, 74.3, 25.8. Anal. Calcd for $C_{14}H_{20}N_2O_2Cl_8W_2$: C, 18.69; H, 2.24; N, 3.11. Found: C, 19.35; H, 2.47; N, 3.69.

Preparation of *p*-$[Cl_5W{\equiv}NC_6H_4N{\equiv}WCl_5][Ph_3P{=}N{=}PPh_3]_2$. $[Ph_3P{=}N{=}PPh_3]Cl$ (1.5 g, 2.6 mmol) was added to a stirred solution of *p*-$[(THF)Cl_4W{=}NC_6H_4N{=}WCl_4(THF)]$ (1.17 g, 1.3 mmol) in CH_2Cl_2 (100 mL). After being stirred for 1 h, the solution was filtered, and the filtrate was evaporated to dryness. The dark green residue was washed with a 1:1 mixture of CH_2Cl_2 and hexane (50 mL) and dried under vacuum to afford the green powdery product (1.8 g; 73% yield). ^1H NMR ($CDCl_3$): δ 7.62 (br, 12 H, $C_6\mathit{H}_5$), 7.45 (br, 48 H, $C_6\mathit{H}_5$), 7.37 (s, 4H, $C_6\mathit{H}_4$). $^{13}C(^1H)$ NMR ($CDCl_3$): δ 133.9, 132.2, 132.0 (d, J_{PC} = 5 Hz), 131.0, 129.7 (d, J_{PC} = 9 Hz), 126.9 (d, J_{PC} = 109 Hz). Anal. Calcd for $C_{78}H_{64}N_4P_4Cl_{10}W_2$: C, 49.21; H, 3.39; N, 2.94. Found: C, 49.75; H, 3.18; N, 2.46.

Preparation of *p*-$[(PhEt_2P)_2Cl_3W{\equiv}NC_6H_4N{\equiv}WCl_3(PEt_2Ph)_2]$. Finely ground *p*-$[(THF)Cl_4W{\equiv}NC_6H_4N{\equiv}WCl_4(THF)]$ (0.70 g, 0.77 mmol) was suspended in toluene (50 mL) and the mixture was stirred vigorously while a toluene solution (10 mL) of $PhEt_2P$ (0.70 g, 4.2 mmol) was added dropwise at room temperature. The reaction mixture was heated at 80 °C for 2 days, after which time the red-brown solution was filtered while still hot. The filtrate was taken to dryness, and the residue was washed with hexane (30 mL). The red-brown solid product was dried under vacuum (0.92 g; 88% yield). ESR ($CDCl_3$): triplet, g = 1.91, $A(^{31}P)$ = 31.9 G. Anal. Calcd for $C_{46}H_{64}N_2P_4Cl_6W_2$: C, 40.95; H, 4.78; N, 2.08. Found: C, 41.36; H, 4.88; N, 2.08.

Preparation of *p*-$[(PhEt_2P)_3Cl_2W{\equiv}NC_6H_4N{\equiv}WCl_2(PEt_2Ph)_3]$. A three-necked flask was charged with *p*-$[L_2Cl_3W{\equiv}NC_6H_4N{\equiv}WCl_3L_2]$ (0.92 g, 0.68 mmol; L = $PhEt_2P$) and 50 mL of toluene. The mixture was warmed to 85 °C to effect complete dissolution (ca. 1 h), and then excess sodium amalgam was added (0.05 g of Na, 2.1 mmol; 2.5 mL of Hg). A solution of $PhEt_2P$ (0.70 g; 4.2 mmol) in toluene (10 mL) was then added dropwise, and the reaction mixture was stirred at 75 °C for 18 h. The dark yellow-brown solution was filtered through a Celite pad, which was eluted with an additional 30 mL of toluene. The combined filtrates were evaporated to dryness under vacuum to yield a solid residue,

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[10] Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988.

which was washed with pentane (2 × 50 mL) and dried to afford the powdery yellow product (0.78 g; 72% yield). ^{1}H NMR ($\mathrm{C_6D_6}$): 7.25 (br, 9 H, $\mathrm{C_6}H_5$), 7.01 (m, 15 H, $\mathrm{C_6}H_5$), 6.95 (m, 3 H, $\mathrm{C_6}H_5$), 6.80 (m, 3 H, $\mathrm{C_6}H_5$), 6.72 (s, 4 H, $\mathrm{C_6}H_4$), 3.18 (m, 4 H, $\mathrm{C}H_2$), 2.62 (m, 4 H, $\mathrm{C}H_2$), 2.29 (m, 4 H, $\mathrm{C}H_2$), 2.08 (m, 4 H, $\mathrm{C}H_2$), 1.99 (m, 4 H, $\mathrm{C}H_2$), 1.76 (m, 4 H, $\mathrm{C}H_2$), 1.36 (m, 12 H, $\mathrm{C}H_3$), 0.87 (m, 12 H, $\mathrm{C}H_3$), 0.74 (m, 12 H, $\mathrm{C}H_3$). ^{31}P(^{1}H) NMR ($\mathrm{C_6D_6}$): δ −2.29 (s, area 1, $J_{\mathrm{WP}} = 378$ Hz), −7.86 (s, area 2, $J_{\mathrm{WP}} = 291$ Hz). Anal. Calcd for $\mathrm{C_{66}H_{94}N_2P_6Cl_4W_2}$: C, 49.21; H, 5.88; N, 1.73. Found: C, 48.99; H, 5.98; N, 1.11.

Preparation of *o*-[$\mathrm{Cl_4W{\equiv}NC_6H_4N{\equiv}WCl_4}$]. A solution of 1,2-$\mathrm{Me_3SiNHC_6H_4NHSiMe_3}$ (1.77 g, 7.01 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL) was added dropwise to a stirred solution of $\mathrm{WCl_6}$ (5.76 g, 14.5 mmol) in 50 mL of $\mathrm{CH_2Cl_2}$. A brownish-green precipitate formed immediately. After the mixture was stirred for 12 h, the insoluble material was collected by filtration, washed with $\mathrm{CH_2Cl_2}$ (3 × 50 mL), and dried under vacuum to yield the dark green product (4.2 g; 79% yield).

Preparation of *o*-[(THF)$\mathrm{Cl_4W{\equiv}NC_6H_4N{\equiv}WCl_4}$(THF)]. *o*-[$\mathrm{Cl_4W{\equiv}NC_6H_4N{\equiv}WCl_4}$] (2.66 g, 3.47 mmol) was added to a minimum amount (ca. 30 mL) of cold (0 °C) THF with stirring. After the mixture was allowed to stand undisturbed for 1 h, the lime green precipitate was collected by filtration, washed with hexane (50 mL), and dried under vacuum (1.87 g; 59% yield). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 7.76 (dd, $J = 6.0$, 3.4 Hz, 2 H, $\mathrm{C_6H_4}$), 7.45 (dd, $J = 6.0$, 3.4 Hz, 2 H, $\mathrm{C_6}H_4$), 4.82 (m, 8 H, $\overline{\mathrm{OC}H_2\mathrm{CH_2CH_2C}H_2}$), 2.19 (m, 8 H, $\overline{\mathrm{OCH_2C}H_2\mathrm{C}H_2\mathrm{CH_2}}$). Anal. Calcd for $\mathrm{C_{14}H_{20}N_2O_2Cl_8W_2}$: C, 18.69; H, 2.24; N, 3.11. Found: C, 18.71; H, 2.28; N, 2.82.

Preparation of *o*-[$\mathrm{(Et_2PhP)_2Cl_3W{\equiv}NC_6H_4N{\equiv}WCl_3(PPhEt_2)_2}$]. Finely ground *o*-[(THF)$\mathrm{Cl_4W{\equiv}NC_6H_4N{\equiv}WCl_4}$(THF)] (1.04 g; 1.16 mmol) was suspended in toluene (50 mL), and the suspension was stirred vigorously while a solution of $\mathrm{PPhEt_2}$ (1.1 g, 6.6 mmol) in toluene (10 mL) was added dropwise at room temperature. The mixture was then maintained at 80 °C for 2 days. The resulting red-brown solution was then filtered while still hot. The filtrate was evaporated under vacuum and the residue was washed with hexane (30 mL), leaving a yellow-brown solid when dried (1.39 g; 83% yield). ESR ($\mathrm{CDCl_3}$): triplet, $g = 1.90$; $A(^{31}\mathrm{P}) = 30.6$ G. Anal. Calcd for $\mathrm{C_{46}H_{64}N_2P_4Cl_6W_2}$: C, 40.95; H, 4.78; N, 2.08. Found: C, 39.67; H, 4.79; N, 2.35.

Preparation of *o*-[$\mathrm{(Me_3P)_2Cl_3W{\equiv}NC_6H_4N{\equiv}WCl_3(PMe_3)_2}$]. Finely ground *o*-[(THF)$\mathrm{Cl_4W{\equiv}NC_6H_4N{\equiv}WCl_4}$(THF)] (0.93 g, 1.03 mmol) was added to toluene (100 mL), and the mixture was stirred for 1 h to achieve a uniformly dispersed suspension. A 1.0 M solution of $\mathrm{Me_3P}$ in toluene (5.4 mL, 5.4 mmol) was then added dropwise to the stirred suspension. After being stirred at room temperature for 5 h, the mixture was heated at 80 °C for 3 days. The resulting red-brown solution was filtered while hot, and the volatile components of the filtrate were removed under vacuum, leaving a light yellow powder. The product was washed with hexane (2 × 100 mL) and dried under vacuum (0.92 g; 90% yield). ESR (toluene, 23 °C): triplet, $g = 1.89$; $A(^{31}\mathrm{P}) = 31.2$ G. Anal. Calcd for $\mathrm{C_{18}H_{40}N_2P_4Cl_6W_2}$: C, 21.86; H, 4.08; N, 2.83. Found: C, 21.82; H, 4.09; N, 2.56.

Preparation of *o*-[$\mathrm{(Et_2PhP)_2Cl_2W{\equiv}NC_6H_4N{\equiv}WCl_2(PPhEt_2)_2}$]. A three-necked flask was charged with *o*-[$\mathrm{(Et_2PhP)_2Cl_3W{\equiv}NC_6H_4N{\equiv}WCl_3(PPhEt_2)_2}$] (1.3 g; 0.96 mmol) and 150 mL of toluene. After being heated to 85 °C for 1 h to effect complete dissolution, the mixture was treated with sodium amalgam (0.05 g of Na, 2.1 mmol; 2.5 mL of Hg). A portion of $\mathrm{Et_2PhP}$ (0.98 g, 5.9 mmol) in toluene (10 mL) was then added dropwise, and the mixture was stirred at 80 °C for 30 h. The yellow-brown solution was filtered through a Celite pad, which was eluted with a further 30 mL of toluene, and the combined filtrates were evaporated under vacuum. The residue was washed with $\mathrm{Et_2O}$ (50 mL) and with hexane (2 × 50 mL) to afford the powdery yellow product, which was dried under vacuum (0.98 g; 80% yield). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 7.47 (m, 8 H, $\mathrm{C_6}H_5$), 7.11 (m, 8 H, $\mathrm{C_6}H_5$), 7.05 (m, 4 H, $\mathrm{C_6}H_5$), 6.87 (dd, 2 H, $\mathrm{C_6}H_4$), 6.06 (dd, 2 H, $\mathrm{C_6}H_4$), 2.24–2.02 (m, 16 H, $\mathrm{C}H_2$), 1.01–0.87 (m, 24 H, $\mathrm{C}H_3$). ^{13}C(^{1}H) NMR ($\mathrm{C_6D_6}$): δ 156.22, 143.58 (d, $J_{\mathrm{PC}} = 37.8$ Hz), 131.37, 128.74, 125.04, 121.72, 22.99 (d, $J_{\mathrm{PC}} = 27.6$ Hz), 22.05 (d, $J_{\mathrm{PC}} = 27.6$ Hz), 8.49. ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 6.28 (s, $J_{\mathrm{WP}} = 412$ Hz). Anal. Calcd for $\mathrm{C_{46}H_{64}N_2P_4Cl_4W_2}$: C, 43.22; H, 5.04; N, 2.19. Found: C, 42.11; H, 4.92; N, 1.69.

Preparation of *o*-[$\mathrm{(Me_3P)_3Cl_2W{\equiv}NC_6H_4N{\equiv}WCl_2(PMe_3)_3}$]. A three-necked flask was charged with *o*-[$\mathrm{Me_3P)_2Cl_3W{\equiv}NC_6H_4N{\equiv}WCl_3(PMe_3)_2}$] (0.40 g, 0.40 mmol) and 50 mL of toluene. The mixture was stirred until complete dissolution occurred (ca. 1 h) and was then treated with sodium amalgam (0.025 g of Na, 1.1 mmol; 1.2 mL of Hg). A portion of a 1.0 M $\mathrm{Me_3P}$/toluene solution (4 mL, 4 mmol) was added dropwise, and the reaction mixture was stirred at room temperature for 12 h, during which time the color gradually changed from red-brown to yellow-brown. Stirring was then discontinued, and the mixture was allowed to stand for an additional 24 h. The mixture was filtered through a Celite pad, which was eluted with additional toluene (50 mL), and the combined filtrates were evaporated to dryness. The resulting yellow powder was washed with pentane (100 mL) and dried under vacuum (0.35 g; 81% yield). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 6.92 (dd, 2 H, $\mathrm{C_6}H_4$), 6.59 (dd, 2 H, $\mathrm{C_6}H_4$), 1.64 (t, 36 H, $J_{\mathrm{PH}} = 3.8$ Hz), 1.41 (d, 18 H, $J_{\mathrm{PH}} = 7.8$ Hz). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 148.73, 140.08, 123.39, 26.38 (d, $J_{\mathrm{PC}} = 26.8$ Hz), 18.31 (t, $J_{\mathrm{PC}} = 12.9$ Hz). ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$): δ −29.50 (s, area 2, $J_{\mathrm{WP}} = 296$ Hz), −34.12 (s, area 1, $J_{\mathrm{WP}} = 357$ Hz). Anal. Calcd for $\mathrm{C_{24}H_{58}N_2P_6Cl_4W_2}$: C, 26.94; H, 5.46; N, 2.62. Found: C, 26.02; H, 5.38; N, 1.12.

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Registry No. $\mathrm{Me_3SiNH}$-1,4-$\mathrm{C_6H_4NHSiMe_3}$, 1571-74-0; $\mathrm{Me_3SiNH}$-1,2-$\mathrm{C_6H_4NHSiMe_3}$, 13435-10-4; $\mathrm{Me_3SiCl}$, 75-77-4; *p*-[$\mathrm{Cl_4W{\equiv}NC_6H_4N{\equiv}WCl_4}$], 139041-55-7; *p*-[(THF)$\mathrm{Cl_4W{\equiv}NC_6H_4N{\equiv}WCl_4}$(THF)], 139041-44-4; *p*-[$\mathrm{Cl_5W{\equiv}NC_6H_4N{\equiv}WCl_5}$][$\mathrm{Ph_3P{=}N{=}PPh_3}$]$_2$, 139041-46-6; *p*-[$\mathrm{(PhEt_2P)_2Cl_3W{\equiv}NC_6H_4N{\equiv}WCl_3(PEt_2Ph)_2}$], 139041-47-7; *p*-[$\mathrm{(PhEt_2P)_3Cl_2W{\equiv}NC_6H_4N{\equiv}WCl_2(PEt_2Ph)_3}$], 139041-48-8; *o*-[$\mathrm{Cl_4W{\equiv}NC_6H_4N{\equiv}WCl_4}$], 139041-49-9; *o*-[(THF)$\mathrm{Cl_4W{\equiv}NC_6H_4N{\equiv}WCl_4}$(THF)], 139041-50-2; *o*-[$\mathrm{(PhEt_2P)_2Cl_3W{\equiv}NC_6H_4N{\equiv}WCl_3(PEt_2Ph)_2}$], 139041-51-3; *o*-[$\mathrm{(Me_3P)_2Cl_3W{\equiv}NC_6H_4N{\equiv}WCl_3(PMe_3)_2}$], 139041-52-4; *o*-{$\mathrm{(Et_2PhP)_2Cl_2W{\equiv}NC_6H_4N{\equiv}WCl_2(PEt_2Ph)_2}$], 139041-53-5; *o*-[$\mathrm{(Me_3P)_3Cl_2W{\equiv}NC_6H_4N{\equiv}WCl_2(PMe_3)_3}$], 139041-54-6; 1,4-phenylenediamine, 106-50-3; 1,2-phenylenediamine, 95-54-5.