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Reactions at Metal-Bound Nitrogen Atoms. Formation of Molybdenum and Tungsten Phosphoraniminato Complexes from Silylimido Complexes and Synthesis of a Nitride-Bridged Tungsten Derivative

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Tungsten(VI) and molybdenum(VI) phosphoraniminato complexes, $M(NPMe_3)Cl_5$, are synthesized in good yield by the reaction of excess Cl_2 with tungsten(IV) and molybdenum(IV) silylimido complexes, $M(NSiMe_3)Cl_2(PMe_3)_3$. These reactions are accompanied by loss of $ClSiMe_3$ and PCl_2Me_3. Related tungsten(IV) and molybdenum(IV) phosphoraniminato complexes, $[W(NPR_3)Cl_2(PMe_3)_3]Cl$ ($PR_3 = PMe_3$, $PMePh_2$, PPh_3) and $[Mo(NPMe_3)Cl_2(PMe_3)_3]Cl$, are readily prepared by addition of PCl_2R_3 to $M(NSiMe_3)Cl_2(PMe_3)_3$. The tungsten(IV) derivatives react with excess Cl_2 producing $W(NPR_3)Cl_5$ and PCl_2Me_3, with subsequent exchange of the P^VR_3 and P^VMe_3 groups occurring. A tungsten(V) phosphoraniminato derivative, $W(NPMe_3)Cl_4(PMe_3)$, is isolated from the reaction of $W(NSiMe_3)Cl_2(PMe_3)_3$ with limited Cl_2 and is found to form by conproportionation of $W(NPMe_3)Cl_5$ and $[W(NPMe_3)Cl_2(PMe_3)_3]Cl$. The tungsten(VI) triphenylphosphoraniminato complex can also be prepared by addition of PCl_2Ph_3 to $W(N)Cl_3$ or from $Me_3SiNPPh_3$ and WCl_6, with additional $Me_3SiNPPh_3$ or $Me_3SiNPMePh_2$ producing bis(phosphoraniminato) complexes. In contrast, attempts to synthesize $W(NPMePh_2)Cl_5$ by the reaction of WCl_6 and $Me_3SiNPMePh_2$ instead result in high-yield formation of a reduced mixed-valence nitride-bridged compound, $[W_2(N)Cl_9]_2[PClMePh_2]_2$. Four of the tungsten phosphoraniminato complexes in this system have been structurally characterized and are found to contain approximately linear WNP geometries with short tungsten–nitrogen multiple-bond distances (1.736–1.791 Å). The nitride-bridged tungsten derivative possesses an asymmetric linear W(N)W structure with one short tungsten–nitrogen bond (1.682 Å) suggesting description of this species as an anionic tungsten(VI) nitride acting as a two-electron ligand to tungsten(V) chloride.

Introduction

The chemistry of transition-metal complexes with organonitrogen ligands—amines, amidos, imidos, and hydrazidos—has been investigated by a number of chemists due to the relevance of these ligands to metal-promoted industrial and biological processes. In comparison, however, transition-metal complexes containing main-group-substituted nitrogen ligands—such as silylimidos (I) and phosphoraniminatos (II)—have received much less attention. We became interested in such derivatives, in

$$\underset{\text{I}}{L_nM(NSiR_3)} \qquad \underset{\text{II}}{L_nM(NPR_3)}$$

particular transition-metal silylimido complexes, when looking for precursors for the synthesis of nitride-bridged transition-metal compounds and materials.[1,2]

We have prepared a number of transition-metal silylimido derivatives and examined their reactions with transition-metal halides; formation of nitride-bridged products occurs readily and in extremely high yield for some silylimido complexes, but not at all for others.[1–4] In order to further develop our understanding of the reactivity available to silylimido complexes, we set out to explore their chemistry with other halogen-containing reagents capable of attacking the nitrogen-silicon bond.[5] We describe here reactions of chlorine and organophosphorus(V) dichlorides with the molybdenum and tungsten complexes $M(NSiMe_3)Cl_2(PR_3)_3$[3] (**1**–**3**). These reactions result in unusual transformations of the silylimido ligands into phosphoraniminato ligands.[6] We also report the synthesis of a mixed-valence nitride-bridged compound, $[W_2(N)Cl_9]_2[PClMePh_2]_2$, unexpectedly formed in attempts to prepare tungsten phosphoraniminato complexes by more standard synthetic methodologies. X-ray structural studies of four of the tungsten phosphoraniminato complexes and of the nitride-bridged compound are reported. In addition, the synthesis and structure of the MNP linkage in phosphoraniminato complexes are discussed.

Experimental Section

General Comments. All reactions and manipulations were performed under standard anhydrous and anaerobic conditions using appropriately dried reagent-grade solvents and chemicals.[7] $W(NSiMe_3)Cl_2(PMe_3)_3$ (**1**),[3] $Mo(NSiMe_3)Cl_2(PMe_3)_3$ (**2**),[3] $W(NSiMe_3)Cl_2(PMePh_2)_3$ (**3**),[3] $W(N)Cl_3$,[8] PCl_2R_3 reagents,[9] and Me_3SiNPR_3 reagents[10] were prepared using known procedures. Chlorine (Matheson, semiconductor grade) was purified by several freeze(−196 °C)–pump–thaw cycles followed by vacuum transfer at −78 °C and was handled using glassware which had been flame-dried under vacuum to eliminate moisture. NMR spectra were recorded on Varian VXR300, Bruker WM500 and AM200, and General Electric OMEGA500 and QE300 spectrometers at ambient temperatures in CD_2Cl_2 solution. Chemical shifts are reported in ppm downfield from $\delta = 0$ for $SiMe_4$ relative to the residual solvent signal (^1H, ^{13}C) or in ppm downfield from $\delta = 0$ for external 85% H_3PO_4 (^{31}P); coupling constants are reported in Hz. Infrared spectra were recorded on Perkin-Elmer 283 or 1600 spectrometers as Nujol mulls and are reported in cm^{-1}. Elemental analyses were carried out by the Canadian Microanalytical Service and Galbraith Laboratories. The labeling scheme in this paper uses **a**, **b**, and **c** to indicate related compounds with $NPMe_3$, $NPMePh_2$, and NPh_3 ligands, respectively.

$W(NPMe_3)Cl_5$ (4a). (a) Cl_2 (0.083 mL, 1.75 mmol) was vacuum transferred onto a solution of **1** (0.245 g, 0.430 mmol) in dichloromethane (10 mL) frozen at −196 °C. The mixture was warmed to 22 °C and stirred for 20 min. The resulting orange solution was decanted away from the crystalline PCl_2Me_3 byproduct and the solution volume reduced, producing an orange precipitate. This was collected by filtration, washed

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repeatedly with cold dichloromethane, and dried under vacuum, yielding 0.112 g of orange crystalline **4a** (58%). (b) **4a** was formed in greater than 90% yield in the orange solution obtained when Cl_2 (9 μL, 0.18 mmol) and blue **6a** (29 mg, 0.048 mmol) were allowed to react at 22 °C in CD_2Cl_2 in a sealed NMR tube. (c) **4a** was formed in greater than 90% yield in the orange solution obtained when green **7a** (2 mg, 0.004 mmol) and excess Cl_2 were allowed to react at 22 °C in CD_2Cl_2 in a sealed NMR tube. ^{1}H NMR: 2.90 (d, J_{PH} = 14). $^{31}P\{^{1}H\}$ NMR: 89.7 (s). IR: 1308, 1303, 1150, 962, 880, 780, 730, 370, 325, 262. Anal. Calcd for $C_3H_9Cl_5NPW$: C, 7.99; H, 2.01; N, 3.10. Found: C, 8.69; H, 2.28; N, 2.90.

$W(NPMePh_2)Cl_5$ (4b). (a) Cl_2 (5 μL, 0.10 mmol) was vacuum transferred onto a solution of **3** (24 mg, 0.027 mmol) in CD_2Cl_2 frozen at −196 °C in an NMR tube. The tube was sealed, and the mixture was warmed to 22 °C and allowed to react for 1 day, producing a clear orange solution containing **4b** in greater than 90% yield. (b) **4b** was formed in the orange solution obtained when Cl_2 (5 μL, 0.10 mmol) and green **6b** (19 mg, 0.026 mmol) were allowed to react at 22 °C in CD_2Cl_2; **4a** was also formed in this reaction, with its concentration in solution increasing over time at the expense of the disappearance of **4b**. ^{1}H NMR: 8.1–7.7 (m, 12 H), 3.26 (d, J_{PH} = 13, 3 H). $^{31}P\{^{1}H\}$ NMR: 71.7 (s).

$W(NPPh_3)Cl_5$ (4c).[11] (a) Dichloromethane (20 mL) was added to a mixture of solid WCl_6 (0.974 g, 2.46 mmol) and $Me_3SiNPPh_3$ (0.836 g, 2.39 mmol) at −78 °C. The resulting yellow mixture was allowed to warm to 22 °C and stirred for 2.5 h, producing a dark orange solution and an orange precipitate. The solvent volume was reduced to 5 mL and the orange solid was collected by filtration, washed with small amounts of cold dichloromethane, and dried under vacuum, yielding 0.959 g of orange crystalline **4c**; a second crop of **4c** (72 mg) can be obtained from the washings using minimal amounts of dichloromethane for a total yield of 66%. (b) **4c** was formed in the orange solution obtained when Cl_2 (3.5 μL, 0.07 mmol) and green **6c** (15 mg, 0.019 mmol) were allowed to react at 22 °C in CD_2Cl_2; **4a** was also formed in this reaction, with its concentration increasing over time at the expense of the disappearance of **4c**. (c) **4c** was detected as the major product in solution when $W(N)Cl_3$ (14 mg, 0.046 mmol) and PCl_2Ph_3 (16 mg, 0.048 mmol) were allowed to react for several days at 22 °C in CD_2Cl_2 in a sealed NMR tube. ^{1}H NMR: 7.92 (m, 9 H), 7.80 (td, J_{HH} = 8, J_{PH} = 4, 6 H). $^{13}C\{^{1}H\}$ NMR: 136.8 (s), 134.7 (d, J_{PC} = 14), 130.9 (d, J_{PC} = 15). $^{31}P\{^{1}H\}$ NMR: 46.1 (s). IR: 1590, 1135, 1000, 730. Anal. Calcd for $C_{18}H_{15}Cl_5NPW$: C, 33.92; H, 2.37; N, 2.20. Found: C, 33.23; H, 2.90; N, 1.97.

$Mo(NPMe_3)Cl_5$ (5a). Cl_2 (0.198 mL, 4.16 mmol) was vacuum transferred onto a solution of **2** (0.249 g, 0.516 mmol) in dichloromethane (10 mL) frozen at −196 °C. The mixture was rapidly warmed to 22 °C and stirred for 5 min. The resulting yellow precipitate was collected by filtration from the green solution, washed repeatedly with cold dichloromethane, and dried under vacuum, yielding 0.178 g of **5a** (95%). ^{1}H NMR: 2.89 (d, J_{PH} = 10). $^{31}P\{^{1}H\}$ NMR: 79.3 (s). IR: 1300, 1290, 1002, 980, 962, 892, 876, 780, 699.

$[W(NPMe_3)Cl_2(PMe_3)_3]Cl$ (6a). (a) Dichloromethane (25 mL) was added to a mixture of solid **1** (0.530 g, 0.930 mmol) and PCl_2Me_3 (0.136 g, 0.925 mmol) at −78 °C. The resulting violet solution turned blue upon warming to 22 °C and was stirred for 12 h. The solvent and volatiles were removed under reduced pressure, and the product was crystallized from dichloromethane/diethyl ether, collected by filtration, washed with diethyl ether, and dried under vacuum, yielding 0.480 g of blue **6a** (85%). (b) **6a** was detected in the mixture of products formed when $W(N)Cl_3$ (10 mg, 0.033 mmol) and PMe_3 (39 Torr in 64.5 mL at 22 °C, 0.14 mmol) were allowed to react for 1 day at 22 °C in CD_2Cl_2 in a sealed NMR tube. ^{1}H NMR: 2.11 (d, J_{PH} = 14, 9 H), 1.90 (d, J_{PH} = 8, 9 H), 1.69 (t, J_{PH} = 4, 18 H). $^{13}C\{^{1}H\}$ NMR: 28.7 (d, J_{PC} = 31), 19.2 (t, J_{PC} = 15), 14.4 (d, J_{PC} = 63). $^{31}P\{^{1}H\}$ NMR: 57.3 (s, J_{WP} = 110), −29.7 (s, J_{WP} = 290), −38.1 (s, J_{WP} = 360). IR: 1298, 1282, 1165, 954, 724, 415, 252, 300, 292, 280, 250, 230. Anal. Calcd for $C_{12}H_{36}Cl_3NP_4W$: C, 23.69; H, 5.96; N, 2.30. Found: C, 23.81; H, 5.64; N, 2.14.

$[W(NPMePh_2)Cl_2(PMe_3)_3]Cl$ (6b). Procedure a for **6a** was followed with **1** (0.410 g, 0.719 mmol) and PCl_2MePh_2 (0.199 g, 0.734 mmol), producing a clear green solution after 5 h at 22 °C. Crystallization from dichloromethane/diethyl ether yielded 0.494 g of green **6b** (94%). ^{1}H NMR: 8.01 (dd, J_{HH} = 7, J_{PH} = 14, 4 H), 7.75 (t, J_{HH} = 7, 2 H), 7.63 (td, J_{HH} = 7, J_{PH} = 4, 4 H), 2.86 (d, J_{PH} = 13, 3 H), 1.86 (d, J_{PH} = 8, 9 H), 1.52 (t, J_{PH} = 4, 18 H). $^{13}C\{^{1}H\}$ NMR: 135.0 (s), 132.8 (d, J_{PC} = 12), 131.5 (d, J_{PC} = 13), 28.9 (d, J_{PC} = 31), 18.9 (t, J_{PC} = 15); the methyl carbon of the $NPMePh_2$ ligand was not found. $^{31}P\{^{1}H\}$ NMR: 41.8 (s, J_{WP} = 120), −35.1 (s, J_{WP} = 290), −42.5 (s, J_{WP} = 360). IR: 1586, 1440, 1303, 1285, 1155, 1116, 951, 906, 795, 731, 698, 532, 510, 291, 255. Anal. Calcd for $C_{22}H_{40}Cl_3NP_4W$: C, 36.07; H, 5.50; N, 1.91. Found: C, 35.77; H, 5.49; N, 1.98.

$[W(NPPh_3)Cl_2(PMe_3)_3]Cl$ (6c). Procedure a for **6a** was followed with **1** (0.404 g, 0.709 mmol) and PCl_2Ph_3 (0.253 g, 0.759 mmol), producing a green solution after 2 h at 22 °C. Crystallization from pentane/diethyl ether (5:1) yielded 0.535 g of green **6c** (95%). ^{1}H NMR: 7.87 (t, J_{HH} = 8, 3 H), 7.72 (td, J_{HH} = 8, J_{PH} = 4, 6 H), 7.58 (dd, J_{HH} = 8, J_{PH} = 13, 6 H), 1.75 (d, J_{PH} = 8, 9 H), 1.49 (t, J_{PH} = 4, 18 H). $^{13}C\{^{1}H\}$ NMR: 135.7 (s), 133.4 (d, J_{PC} = 12), 130.4 (d, J_{PC} = 13), 29.2 (d, J_{PC} = 33), 19.2 (t, J_{PC} = 15). $^{31}P\{^{1}H\}$ NMR: 38.3 (s, J_{WP} = 110), −39.7 (s, J_{WP} = 280), −45.5 (s, J_{WP} = 360). IR: 1550, 1150, 1115, 950, 729, 697. Anal. Calcd for $C_{27}H_{42}Cl_3NPW$: C, 40.81; H, 5.33; N, 1.76. Found: C, 40.51; H, 5.43; N, 1.82.

$W(NPMe_3)Cl_4(PMe_3)$ (7a). (a) Cl_2 (0.09 mL, 1.89 mmol) was vacuum transferred onto a solution of **1** (0.263 g, 0.461 mmol) in dichloromethane (12 mL) frozen at −196 °C. The mixture was rapidly warmed to 22 °C and stirred for 10 min, and the excess Cl_2 was removed under vacuum, producing a green solution containing a small amount of orange precipitate. The orange precipitate was collected by filtration, washed with dichloromethane, and dried under vacuum, yielding 55 mg of orange **4a** (26%). The green residue obtained after removing the solvent and volatiles from the supernatant was crystallized from dichloromethane/tetrahydrofuran (1:2), collected by filtration, and dried under vacuum, yielding 0.155 g of green crystalline **7a** (69%). (b) A green solution of **7a** was formed immediately from orange **4a** (10 mg, 0.022 mmol) and blue **6a** (14 mg, 0.023 mmol) at 22 °C in CD_2Cl_2 in a sealed NMR tube. The green crystals that slowly formed in this sample over 1 month at 22 °C were collected by filtration, washed with dichloromethane, and dried under vacuum, yielding 9 mg of **7a** (84%). IR: 1297, 1173, 948, 873, 310, 285. Anal. Calcd for $C_6H_{18}Cl_4NP_2W$: C, 14.65; H, 3.69; N, 2.85. Found: C, 14.71; H, 3.68; N, 2.71.

$[Mo(NPMe_3)Cl_2(PMe_3)_3]Cl$ (8a).[12] Green **8a** was formed in greater than 90% yield when **2** (21 mg, 0.044 mmol) and PCl_2Me_3 (7 mg, 0.048 mmol) were allowed to react for 3 h at 22 °C in CD_2Cl_2 in a sealed NMR tube. ^{1}H NMR: 2.15 (d, J_{PH} = 14, 9 H), 1.77 (d, J_{PH} = 8, 9 H), 1.65 (t, J_{PH} = 4, 18 H). $^{31}P\{^{1}H\}$ NMR: 58.0 (s), −0.4 (t, J_{PP} = 17), −4.9 (d, J_{PP} = 17).

$W(NPMePh_2)(NPPh_3)Cl_4$ (9b). **9b** was formed as the major tungsten-containing product in the yellow solution obtained when **4c** (10 mg, 0.016 mmol) and $Me_3SiNPMePh_2$ (0.5 mL of a 48.7 mM CD_2Cl_2 solution, 0.024 mmol) were allowed to react for 3 h at 22 °C in a sealed NMR tube. ^{1}H NMR: 7.78 (dd, J_{HH} = 8, J_{PH} = 14), 7.65 (m), 7.51 (td, J_{HH} = 8, J_{PH} = 4), 2.65 (d, J_{PH} = 14); integrals could not be measured due to overlap with the signals of the excess $Me_3SiNPMePh_2$ present. $^{31}P\{^{1}H\}$ NMR: 37.2 (s, J_{WP} = 110), 33.1 (s, J_{WP} = 100).

$W(NPPh_3)_2Cl_4$ (9c).[11] Dichloromethane (23 mL) was added to a mixture of solid **4c** (0.462 g, 0.725 mmol) and $Me_3SiNPPh_3$ (0.253 g, 0.724 mmol) at 22 °C. The mixture was stirred for 1 day, the solvent volume was reduced to 5 mL, and the resulting yellow precipitate was collected by filtration, washed with acetonitrile, and dried under vacuum, yielding 0.438 g of **9c** (69%). ^{1}H NMR: 7.72 (m, 18 H), 7.48 (td, J_{HH} = 8, J_{PH} = 4, 12 H). $^{31}P\{^{1}H\}$ NMR: 32.8 (s, J_{WP} = 110). IR: 1217, 1100, 750, 725, 690.

$[W_2(\mu\text{-}N)Cl_9]_2[PClMePh_2]_2$ (10). A CD_2Cl_2 solution of $Me_3SiNPMePh_2$ (0.4 mL, 0.18 M, 0.072 mmol) was added to a CD_2Cl_2 solution of WCl_6 (0.3 mL, 0.28 M, 0.084 mmol) and the mixture sealed in an NMR tube. The orange-colored solution turned black in a few hours at 22 °C and was allowed to react for 6 days until crystallization of the reaction product was observed. Black needles were collected by filtration, washed with dichloromethane (2 × 1 mL), and dried under vacuum, yielding 32 mg of crystalline **10** (81%). IR: 1585, 1438, 1340, 1312, 1118, 998, 901, 890, 791, 748, 738, 697, 682, 613, 568, 475, 370, 345, 320. Anal. Calcd for $C_{26}H_{26}Cl_{20}N_2P_2W_4$: C, 16.67; H, 1.40; N, 1.50. Found: C, 16.93; H, 1.59; N, 1.58.

X-ray Diffraction Studies. Crystals were either mounted in a glass capillary under N_2 (room-temperature structures) or oil-mounted on a glass fiber under a stream of cold N_2 (low-temperature structures). The determinations of Laue symmetries, crystal classes, unit cell parameters, and crystal orientation matrices were carried out by methods similar to those previously described by Churchill.[13] Intensity data were collected with graphite-monochromated Mo Kα radiation using a θ–2θ scan technique on an Enraf-Nonius CAD4 diffractometer or a Wyckoff scan technique on a Siemens R3m/V diffractometer. All data were corrected

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(11) Preparation of **4c** and **9c** from WCl_6 and $Me_3SiNPPh_3$ is cited as unpublished work in ref 6. A related reaction of $WMeCl_5$ with $Me_3SiNPPh_3$ producing $W(NPPh_3)MeCl_4$ has also been reported. Roesky, H. W.; Tojo, T.; Ilemann, M.; Westhoff, D. *Z. Naturforsch.* **1987**, *42B*, 877–880.

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Table I. Selected Bond Distances (Å) and Angles (deg) for $W(NPMe_3)Cl_5$ (**4a**), $[W(NPMe_3)Cl_2(PMe_3)_3]Cl$·toluene (**6a**·toluene), $[W(NPMePh_2)Cl_2(PMe_3)_3]Cl$·2MeCN (**6b**·2MeCN), and $W(NPMe_3)Cl_4(PMe_3)$·2MeCN (**7a**·2MeCN)

	4a	**6a**·toluene	**6b**·2MeCN	**7a**·2MeCN
W–N	1.736 (18)	1.789 (3)	1.791 (4)	1.753 (12)
N–P	1.668 (19)	1.628 (3)	1.630 (4)	1.625 (13)
$W–Cl_{trans}$	2.465 (7)	2.473 (1)	2.441 (2)	2.458 (5)
$W–Cl_{cis}/P_{cis}$	2.306 (7) (Cl)	2.491 (1) (Cl)	2.507 (1) (Cl)	2.360 (9) (Cl)
	2.339 (7) (Cl)	2.470 (1) (P)	2.488 (1) (P)	2.407 (4) (Cl)
	2.328 (8) (Cl)	2.493 (1) (P)	2.515 (1) (P)	2.366 (10) (Cl)
	2.328 (8) (Cl)	2.495 (1) (P)	2.519 (1) (P)	2.531 (4) (P)
W–N–P	164.1 (12)	164.2 (2)	171.0 (3)	163.1 (13)
$N–W–Cl_{trans}$	172.2 (6)	177.0 (1)	178.2 (1)	171.2 (7)
$N–W–Cl_{cis}/P_{cis}$	98.5 (6) (Cl)	93.8 (1) (Cl)	95.9 (1) (Cl)	100.6 (8) (Cl)
	89.8 (6) (Cl)	88.2 (1) (P)	90.9 (1) (P)	96.9 (4) (Cl)
	91.0 (6) (Cl)	100.8 (1) (P)	97.6 (1) (P)	88.4 (8) (Cl)
	99.0 (6) (Cl)	102.5 (1) (P)	97.4 (1) (P)	91.4 (4) (P)

Table II. Selected Bond Distances (Å) and Angles (deg) for $[W_2(N)Cl_9]_2[PClMePh_2]_2$ (**10**)

W(1)–N(1)	1.682 (10)	W(2)–N(1)	2.050 (10)
W(1)–Cl(1)	2.848 (3)	W(2)–Cl(5)	2.297 (5)
W(1)–Cl(1′)	2.392 (4)	W(2)–Cl(6)	2.278 (5)
W(1)–Cl(2)	2.307 (4)	W(2)–Cl(7)	2.329 (4)
W(1)–Cl(3)	2.287 (4)	W(2)–Cl(8)	2.286 (5)
W(1)–Cl(4)	2.288 (4)	W(2)–Cl(9)	2.321 (4)
W(1)–N(1)–W(2)	177.6 (6)	W(1)–Cl(1)–W(1′)	101.7 (1)
N(1)–W(1)–Cl(1)	174.6 (4)	N(1)–W(2)–Cl(5)	87.4 (3)
N(1)–W(1)–Cl(1′)	96.3 (4)	N(1)–W(2)–Cl(6)	87.5 (4)
N(1)–W(1)–Cl(2)	97.6 (4)	N(1)–W(2)–Cl(7)	88.0 (3)
N(1)–W(1)–Cl(3)	100.1 (4)	N(1)–W(2)–Cl(8)	87.5 (4)
N(1)–W(1)–Cl(4)	98.3 (4)	N(1)–W(2)–Cl(9)	180.0 (6)

for absorption and for Lorentz and polarization effects. Computations were carried out using either the UCI-modified version of the UCLA Crystallographic Computing Package[14] or the SHELXTL PLUS program set.[15] The analytical scattering factors for neutral atoms were used throughout the analysis; both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion[16] were included. The structures were solved by Patterson or direct methods and refined by full-matrix least-squares techniques. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$. Hydrogen atoms were included using a riding model. Selected bond distances and angles are listed in Tables I and II. Crystallographic data are summarized in Table III. Atomic coordinates and equivalent isotropic displacement coefficients for non-hydrogen atoms of the metal complexes are given in Tables IV–VIII.

Structure Determination for $W(NPMe_3)Cl_5$ (4a). Crystals were obtained from the reaction of **1** and excess Cl_2 in CD_2Cl_2 in a sealed NMR tube. A total of 2476 reflections with $4.0 \le 2\theta \le 50.0°$ were collected on an Enraf-Nonius CAD4 diffractometer. The CAD4 data were converted to the SHELX format using the program XCAD4,[15] and an absorption correction was applied using XABS.[17] The systematic extinctions observed were consistent with the space groups *Pnma* and *Pna*2$_1$; the noncentrosymmetric space group was determined to be correct based on divergence of the model in *Pnma*, intensity statistics of the data, and refinement of the Rogers parameter.[18] Refinement of positional and thermal parameters (anisotropic for all non-hydrogen atoms) led to convergence (GOF = 1.10) for 100 variables refined against those 859 data with $|F_o| > 4.0\sigma(|F_o|)$.

Structure Determination for $[W(NPMe_3)Cl_2(PMe_3)_3]Cl$·toluene (6a·toluene). Crystals of the solvate were obtained by layering toluene onto a solution of **6a** in dichloromethane. A total of 7685 reflections with $4.0 \le 2\theta \le 55.0°$ were collected on a Siemens R3m/V diffractometer. A semiempirical absorption correction was applied using the ψ-scan method. Refinement of positional and thermal parameters (anisotropic for all non-hydrogen atoms) led to convergence (GOF = 1.07) for 254 variables refined against those 6075 data with $|F_o| > 3.0\sigma(|F_o|)$.

Structure Determination for $[W(NPMePh_2)Cl_2(PMe_3)_3]Cl$·2MeCN (6b·2MeCN). Crystals of the solvate were obtained by vapor diffusion of tetrahydrofuran into a solution of **6b** in acetonitrile. A total of 7052 reflections with $4.0 \le 2\theta \le 50.0°$ were collected on a Siemens R3m/V diffractometer. A semiempirical absorption correction was applied using the ψ-scan method. Refinement of positional and thermal parameters (anisotropic for all non-hydrogen atoms) led to convergence (GOF = 1.28) for 335 variables refined against those 5626 data with $|F_o| > 3.0\sigma(|F_o|)$.

Structure Determination for $W(NPMe_3)Cl_4(PMe_3)$·2MeCN (7a·2MeCN). Crystals of the solvate were obtained by vapor diffusion of diethyl ether into a solution of **7a** in acetonitrile. A total of 2557 reflections with $2.0 \le 2\theta \le 55.0°$ were collected on an Enraf-Nonius CAD4 diffractometer. The CAD4 data were converted to the SHELX format using the program XCAD4,[15] and a semiempirical absorption correction was applied using the ψ-scan method. The structure was solved in the space group *P*2$_1$; the absolute structure could not be determined from the diffraction experiment either by refinement of the Rogers parameter[18] or by inversion of the model. Refinement of positional and thermal parameters (anisotropic for W, Cl, and P atoms; isotropic for C and N atoms) led to convergence with (GOF = 2.72) for 116 variables refined against those 2234 data with $|F_o| > 6.0\sigma(|F_o|)$.

Structure Determination for $[W_2(\mu\text{-}N)Cl_9]_2[PClMePh_2]_2$ (10). Crystals were obtained from the reaction of WCl_6 and $Me_3SiNPMePh_2$ in CD_2Cl_2 in a sealed NMR tube. A total of 4449 reflections with $2.0 \le 2\theta \le 55.0°$ were collected on an Enraf-Nonius CAD4 diffractometer. The CAD4 data were converted to the SHELX format using the program XCAD4,[15] and an absorption correction was applied using XABS.[17] Refinement of positional and thermal parameters (anisotropic for all non-hydrogen atoms) led to convergence (GOF = 1.54) for 244 variables refined against those 3527 data with $|F_o| > 4.0\sigma(|F_o|)$.

Results and Discussion

Formation of Tungsten(VI) and Molybdenum(VI) Phosphoraniminato Complexes from Silylimido Complexes and Cl_2. The tungsten(IV) and molybdenum(IV) silylimido complexes $W(NSiMe_3)Cl_2(PMe_3)_3$ (**1**) and $Mo(NSiMe_3)Cl_2(PMe_3)_3$ (**2**) react with excess chlorine gas in dichloromethane over a 20-min period at room temperature to yield tungsten(VI) and molybdenum(VI) phosphoraniminato complexes, $W(NPMe_3)Cl_5$ (**4a**) and $Mo(NPMe_3)Cl_5$ (**5a**) (eq 1). These reactions produce chlorotrimethylsilane, detected by ^1H NMR, and a white insoluble material identified as PCl_2Me_3 by comparison of its IR spectrum to an authentic sample. $W(NSiMe_3)Cl_2(PMePh_2)_3$ (**3**) reacts similarly with excess chlorine in dichloromethane to form $W(NPMePh_2)Cl_5$ (**4b**) (eq 1).

$$M(NSiMe_3)Cl_2(PR_3)_3 + xs\ Cl_2 \xrightarrow[-PCl_2R_3]{-ClSiMe_3} M(NPR_3)Cl_5 \qquad (1)$$

$$\begin{array}{lll} \mathbf{1} & M = W, PR_3 = PMe_3 & \mathbf{4a} \\ \mathbf{2} & M = Mo, PR_3 = PMe_3 & \mathbf{5a} \\ \mathbf{3} & M = W, PR_3 = PMePh_2 & \mathbf{4b} \end{array}$$

Orange **4a,b** and yellow **5a** are generated in good concentrations in dichloromethane solution by reaction 1, allowing their characterization by ^1H and ^{31}P NMR spectroscopy of the reaction mixtures. (After **4a** and **5a** are isolated as crystalline solids, they are only sparingly soluble in organic solvents.) A single broadened low-field resonance is found in the ^{31}P NMR spectra for these compounds, and a doublet shifted to low field with relatively large

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Table III. Crystallographic Data for $W(NPMe_3)Cl_5$ (**4a**), $[W(NPMe_3)Cl_2(PMe_3)_3]Cl \cdot$toluene (**6a**·toluene), $[W(NPMePh_2)Cl_2(PMe_3)_3]Cl \cdot 2MeCN$ (**6b**·2MeCN), $W(NPMe_3)Cl_4(PMe_3) \cdot 2MeCN$ (**7a**·2MeCN), and $[W_2(N)Cl_9]_2[PClMePh_2]_2$ (**10**)

	4a	**6a**·toluene	**6b**·2MeCN	**7a**·2MeCN	**10**
formula	$C_3H_9NPCl_5W$	$C_{19}H_{44}NP_4Cl_3W$	$C_{26}H_{46}N_3P_4Cl_3W$	$C_{10}H_{24}N_3P_2Cl_4W$	$C_{26}H_{26}N_2P_2Cl_{20}W_4$
fw	451.2	700.7	814.8	573.9	1872.8
space group	$Pna2_1$	$P2_1/c$	$P2_1/c$	$P2_1$	$P2_1/c$
a, Å	15.6204 (19)	14.0809 (13)	10.290 (2)	9.256 (3)	11.7802 (16)
b, Å	6.6100 (7)	11.2620 (8)	11.007 (2)	12.360 (5)	14.413 (2)
c, Å	11.4625 (19)	19.871 (2)	31.408 (7)	9.511 (3)	14.977 (3)
β, deg	90	105.415 (8)	91.38 (2)	101.29 (3)	93.096 (15)
V, Å^3	1183.5 (5)	3037.8 (5)	3556.2 (13)	1067.0 (6)	2539.2 (8)
Z	4	4	4	2	2
T, °C	25	−90	−100	23	24
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073
D_{calcd}, g cm^{-3}	2.532	1.532	1.522	1.786	2.450
μ, mm^{-1}	11.196	4.367	3.743	6.179	10.382
$R(F_o)^a$	4.1%	2.9%	3.6%	5.4%	5.7%
$R_w(F_o)^b$	4.3%	3.5%	4.7%	5.9%	6.9%

[a] $R(F_o) = (100\%)\sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F_o) = (100\%)[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w^{-1} = \sigma^2|F_o| + g|F_o|^2$.

Table IV. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for the Non-Hydrogen Atoms of $W(NPMe_3)Cl_5$ (**4a**)

atom	x	y	z	U
W(1)	1834.3 (4)	509.2 (11)	2500	34.0 (2)
Cl(1)	1754 (4)	3397 (10)	3623 (8)	58 (2)
Cl(2)	2438 (4)	2466 (9)	1012 (7)	52 (2)
Cl(3)	1690 (5)	−2259 (10)	1260 (8)	70 (3)
Cl(4)	1039 (4)	−1118 (10)	3938 (8)	60 (2)
Cl(5)	448 (4)	1496 (10)	1644 (8)	58 (2)
P(1)	3806 (3)	−1401 (9)	2965 (7)	33 (2)
N(1)	2850 (12)	−281 (25)	2912 (16)	42 (6)
C(1)	4415 (13)	20 (31)	4000 (25)	44 (8)
C(2)	4220 (17)	−1178 (43)	1547 (22)	56 (9)
C(3)	3708 (16)	−3964 (32)	3352 (25)	62 (10)

Table V. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for the Non-Hydrogen Atoms in the Metal Complex of $[W(NPMe_3)Cl_2(PMe_3)_3]Cl \cdot$toluene (**6a**·toluene)

atom	x	y	z	U
W(1)	7303 (1)	2340 (1)	5307 (1)	182 (1)
Cl(1)	6392 (1)	3814 (1)	4455 (1)	303 (3)
Cl(2)	6448 (1)	722 (1)	4523 (1)	365 (3)
P(1)	8496 (1)	159 (1)	6374 (1)	244 (3)
P(2)	5756 (1)	2526 (1)	5683 (1)	312 (3)
P(3)	8148 (1)	3995 (1)	6042 (1)	241 (3)
P(4)	8368 (1)	2528 (1)	4489 (1)	262 (3)
N(1)	7991 (2)	1338 (3)	5953 (2)	214 (9)
C(1)	8036 (4)	−1097 (3)	5844 (3)	495 (17)
C(2)	9797 (3)	233 (3)	6549 (2)	292 (13)
C(3)	8207 (3)	0 (4)	7190 (2)	403 (15)
C(4)	5426 (3)	3990 (4)	5927 (3)	498 (19)
C(5)	5732 (4)	1602 (5)	6424 (3)	586 (22)
C(6)	4636 (3)	2092 (5)	5033 (3)	557 (20)
C(7)	7855 (4)	5500 (4)	5721 (3)	461 (17)
C(8)	8017 (4)	4070 (5)	6930 (2)	461 (17)
C(9)	9487 (3)	3949 (4)	6268 (2)	337 (14)
C(10)	9524 (4)	1705 (4)	4758 (3)	471 (18)
C(11)	8784 (3)	3985 (4)	4292 (2)	394 (16)
C(12)	7835 (4)	1982 (5)	3612 (2)	522 (19)

proton-phosphorus coupling is observed by ^{1}H NMR spectroscopy for the methyl protons of the phosphoraniminato ligand. Infrared spectroscopy is useful in identifying phosphoraniminato complexes because of the appearance of an intense band in the 1000–1200-cm^{-1} region arising from the MNP linkage.[6] The infrared spectrum of **4a** displays a strong band at 1150 cm^{-1} which can be assigned to ν_{WNP}. In contrast, in the IR spectrum of **5a**, the appearance of two intense bands near 1000 cm^{-1} arising from the MNP and PMe$_3$ groups prevents the unequivocal assignment of ν_{MoNP}.

An X-ray crystallographic study indicates that **4a** possesses a roughly octahedral structure in the solid state (Figure 1) with distances and angles (Table I) in the range reported for other

Table VI. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for the Non-Hydrogen Atoms in the Metal Complex of $[W(NPMePh_2)Cl_2(PMe_3)_3]Cl \cdot 2MeCN$ (**6b**·2MeCN)

atom	x	y	z	U
W(1)	3112 (1)	903 (1)	3317 (1)	193 (1)
Cl(1)	1583 (1)	741 (1)	2686 (1)	320 (4)
Cl(2)	4841 (1)	812 (1)	2799 (1)	335 (4)
P(1)	4843 (1)	1029 (1)	3882 (1)	241 (4)
P(2)	3296 (1)	−1375 (1)	3296 (1)	276 (4)
P(3)	3281 (1)	3142 (1)	3161 (1)	262 (4)
P(4)	590 (1)	1100 (1)	3999 (1)	196 (3)
N(1)	1876 (4)	1000 (3)	3707 (1)	222 (12)
C(1)	6503 (5)	1015 (5)	3702 (2)	351 (18)
C(2)	4825 (5)	2367 (5)	4223 (2)	371 (18)
C(3)	4878 (5)	−138 (5)	4293 (2)	375 (18)
C(4)	4915 (6)	−1997 (5)	3262 (2)	419 (19)
C(5)	2616 (5)	−2134 (5)	3756 (2)	322 (16)
C(6)	2463 (6)	−2158 (5)	2849 (2)	432 (19)
C(7)	2485 (6)	3647 (5)	2669 (2)	414 (19)
C(8)	4897 (6)	3757 (5)	3113 (2)	369 (18)
C(9)	2576 (6)	4143 (4)	3558 (2)	323 (17)
C(10)	−332 (5)	−268 (4)	3929 (2)	231 (14)
C(11)	−943 (5)	−800 (4)	4272 (2)	299 (16)
C(12)	−1697 (6)	−1839 (5)	4204 (2)	378 (18)
C(13)	−1820 (5)	−2349 (5)	3805 (2)	366 (18)
C(14)	−1212 (5)	−1819 (5)	3467 (2)	356 (17)
C(15)	−478 (5)	−772 (4)	3520 (2)	293 (16)
C(16)	−345 (4)	2382 (4)	3813 (2)	232 (14)
C(17)	−1030 (5)	3092 (4)	4097 (2)	306 (16)
C(18)	−1777 (6)	4057 (5)	3939 (2)	362 (18)
C(19)	−1794 (5)	4312 (5)	3509 (2)	364 (18)
C(20)	−1139 (5)	3594 (5)	3226 (2)	358 (17)
C(21)	−405 (5)	2625 (5)	3376 (2)	306 (16)
C(22)	1006 (5)	1297 (5)	4550 (2)	267 (15)

Table VII. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for the Non-Hydrogen Atoms in the Metal Complex of $W(NPMe_3)Cl_4(PMe_3) \cdot 2MeCN$ (**7a**·2MeCN)

atom	x	y	z	U
W(1)	1563 (1)	2500	3468 (1)	37 (1)
Cl(1)	1519 (7)	659 (7)	4117 (10)	81 (3)
Cl(2)	4212 (4)	2497 (14)	3852 (5)	65 (2)
Cl(3)	1820 (6)	2919 (8)	6032 (5)	84 (3)
Cl(4)	1506 (7)	4404 (8)	3205 (7)	74 (2)
P(1)	1360 (4)	2527 (11)	−78 (4)	48 (1)
P(2)	−1173 (4)	2459 (14)	3459 (5)	47 (1)
N(1)	1241 (13)	2392 (20)	1595 (13)	49 (4)
C(1)	818 (27)	1326 (19)	−1070 (24)	67 (6)
C(2)	3194 (24)	2915 (19)	−79 (26)	85 (8)
C(3)	182 (26)	3617 (21)	−795 (24)	76 (7)
C(4)	−2180 (45)	3637 (34)	2724 (39)	135 (17)
C(5)	−1704 (20)	2325 (21)	5203 (19)	67 (6)
C(6)	−2085 (30)	1378 (20)	2441 (27)	61 (7)

Table VIII. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for the Metal Complex of $[W_2(N)Cl_9]_2[PClMePh_2]_2$ (**10**)

atom	*x*	*y*	*z*	*U*
W(1)	9174 (1)	8979 (1)	9286 (1)	39 (1)
W(2)	7293 (1)	6940 (1)	9623 (1)	42 (1)
Cl(1)	10641 (3)	10542 (2)	9185 (2)	45 (1)
Cl(2)	10875 (3)	8204 (2)	9536 (3)	56 (1)
Cl(3)	9329 (4)	8876 (3)	7773 (3)	65 (2)
Cl(4)	7822 (3)	10110 (2)	9087 (3)	56 (1)
Cl(5)	5758 (5)	7890 (3)	9307 (4)	95 (2)
Cl(6)	7480 (6)	6610 (4)	8150 (3)	99 (2)
Cl(7)	8942 (4)	6087 (3)	9949 (4)	76 (2)
Cl(8)	7263 (5)	7350 (4)	11096 (3)	90 (2)
Cl(9)	6151 (4)	5652 (3)	9820 (3)	75 (2)
N(1)	8304 (9)	8076 (6)	9448 (8)	45 (4)

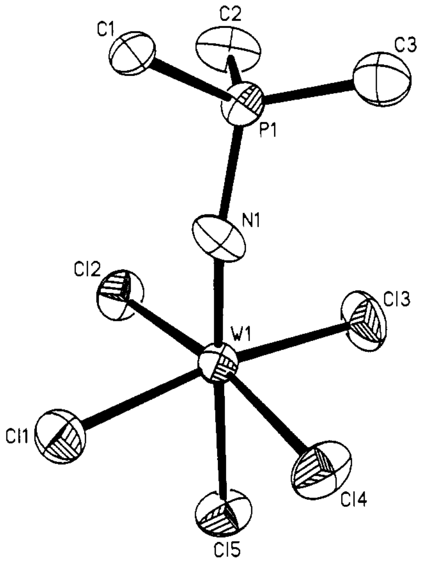
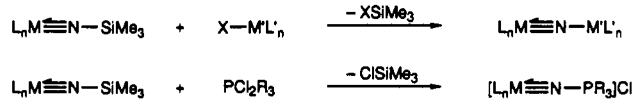


Figure 1. ORTEP drawing of $W(NPMe_3)Cl_5$ (**4a**) with 50% probability thermal ellipsoids for non-hydrogen atoms.

structurally characterized phosphoraniminato complexes.[6,19] Several different $M(NPR_3)$ resonance structures can be considered to describe the bonding between metals and phosphoraniminato ligands. These include linear and bent MNP frameworks with varying degrees of metal–nitrogen and nitrogen–phosphorus multiple bonding.[6,19] Almost without exception, structures of phosphoraniminato complexes are interpreted as having metal–nitrogen and nitrogen–phosphorus double bonds, $L_nM{=}N{=}PR_3$, based on the M–N and N–P distances. Notably absent from literature reports is consideration of structures containing metal–nitrogen triple bonds, $L_nM{\equiv}N{-}PR_3$, in spite of the fact that many phosphoraniminato complexes (e.g., **4** and **5**) contain a high-valent metal center with a pair of degenerate empty orthogonal d-orbitals available for π-bonding. We have recently argued that the shortened N–P distances observed in phosphoraniminato ligands, typically midway between the values quoted for N–P single and double bonds (ca. 1.77 Å and ca. 1.57 Å, respectively[20]), can be rationalized as arising because of sp-hybridization of the nitrogen atom.[5] This appears to be the case in the structure of **4a**, which has a N–P bond distance of 1.668 (19) Å and a short W–N distance (1.736 (18) Å) well within the range reported for tungsten(VI) monoimido complexes possessing W–N triple bonds (ca. 1.66–1.76 Å).[21a] Distortions from idealized octahedral geometry in **4a** further support description of the structures as $Cl_5W{\equiv}N{-}PR_3$; the cis chlorides are bent away from the phosphoraniminato ligand, and the bond to the trans chloride is elongated.[21b]

Scheme I



It is interesting to consider how **4** and **5** are formed upon reaction of **1** and **2** with chlorine. Overall 4 equiv of Cl_2 are required to perform a two-electron oxidation of the metal center and two-electron oxidations of each of three phosphorus atoms, with two PR_3 ligands oxidized to PCl_2R_3 and the third PR_3 oxidized via formation of the phosphoraniminato ligand. Initial attack of chlorine might occur at the silylimido ligand to produce a nitrido species (an as yet unprecedented reaction), which could then add PR_3 to yield the phosphoraniminato group. The latter reaction has been observed in the addition of phosphines to several isolated nitrido compounds.[6,19] However, because phosphines are rapidly chlorinated under the conditions of reaction 1, it would be necessary to invoke migration of PR_3 from the metal to the nitrogen without the intermediacy of any free phosphine in this case. In light of the more precedented observation of attack of external phosphine ligands on nitrido and oxo ligands,[21c] this would be unusual. Chlorination of the silylimido group to produce a chloroimido species can be proposed, as observed in the reaction of $V(NSiMe_3)Cl_3$ with Cl_2 yielding $[V(NCl)Cl_3]_2$.[5] However, we have no precedence for suggesting conversion of a chloroimido compound into a phosphoraniminato compound; instead, the reverse of this reaction is observed[22] for the tungsten system described here. Alternatively, initial attack of chlorine on **1** and **2** could be envisioned to occur at PR_3, either free or coordinated, producing PCl_2R_3, which could subsequently react with the silylimido group. In order to explore the latter possibility, the addition of organophosphorus(V) dichlorides to **1** and **2** was examined.

Synthesis of Tungsten(IV) Phosphoraniminato Complexes Using PCl_2R_3. Tungsten(IV) phosphoraniminato compounds, $[W(NPR_3)Cl_2(PMe_3)_3]Cl$ (**6a–c**), are produced in high yield by the reactions of **1** with PCl_2R_3 in dichloromethane (eq 2). In contrast

$$\underset{\mathbf{1}}{W(NSiMe_3)Cl_2(PMe_3)_3} + PCl_2R_3 \xrightarrow{-ClSiMe_3} [W(NPR_3)Cl_2(PMe_3)_3]Cl \quad (2)$$

$$PR_3 = PMe_3,\ \mathbf{6a}$$
$$PR_3 = PMePh_2,\ \mathbf{6b}$$
$$PR_3 = PPh_3,\ \mathbf{6c}$$

the reaction of $W(NSiMe_3)Cl_2(PMePh_2)_3$ (**3**) with PCl_2R_3 in CD_2Cl_2 does not yield tungsten(IV) phosphoraniminato products on the time scale of the decomposition of **3** in this solvent.

Reaction 2 can be considered a main-group analogue of the formation of bimetallic nitride-bridged complexes by the reaction of metal silylimido complexes with metal halides[1,2] (Scheme I). Both of these transformations are net condensation reactions in which elimination of $XSiMe_3$ occurs, and both yield products in which the transition metal from the starting silylimido complex and the electropositive atom from the halide source are bridged by the nitrogen atom.

Spectral data for **6a–c** indicate that these are diamagnetic compounds[23] possessing a cis meridional structure for the $[M(NPR_3)Cl_2(PMe_3)_3]^+$ cation, analogous to the structures of **1–3**, with the three PMe_3 groups coordinated to the metal center and the PR_3 group in the phosphoraniminato ligand. Single-crystal X-ray diffraction studies on solvates of **6a** and **6b** confirm this connectivity (Figures 2 and 3). These structures have N–P bonds

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(23) NMR spectra of CH_2Cl_2 in CD_2Cl_2 versus a 0.1 M solution of **6** in the same solvent mixture in a coaxial NMR tube showed no discernible shift of the solvent signal, indicating diamagnetic behavior for **6**. (See: Evans, D. F. *J. Chem. Soc.* **1959**, 2003.)

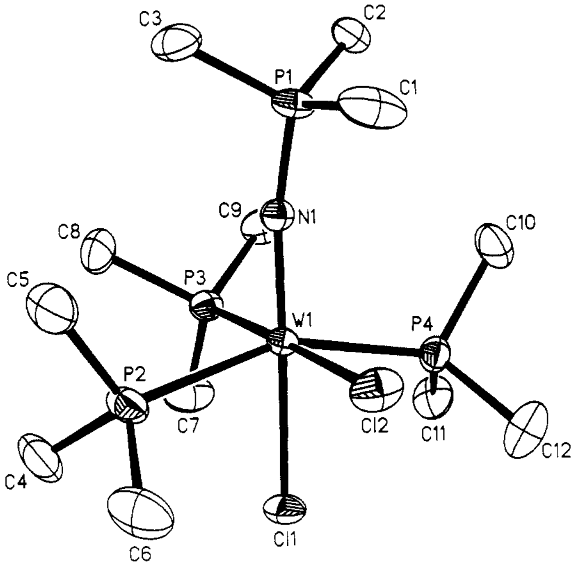


Figure 2. ORTEP drawing of $[W(NPMe_3)Cl_2(PMe_3)_3]^+$ from **6a**·toluene with 50% probability thermal ellipsoids for non-hydrogen atoms.

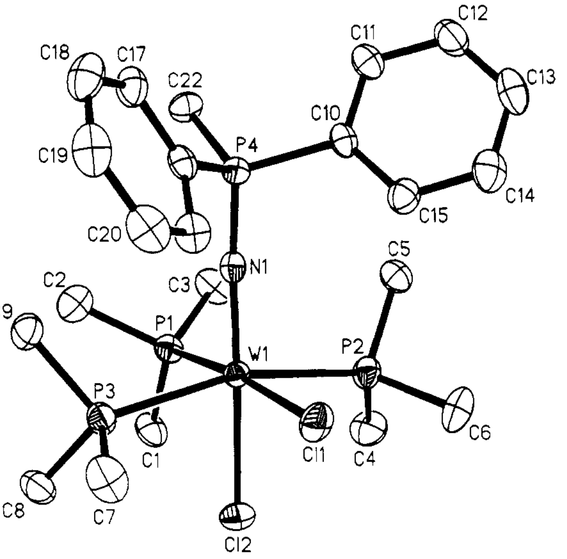
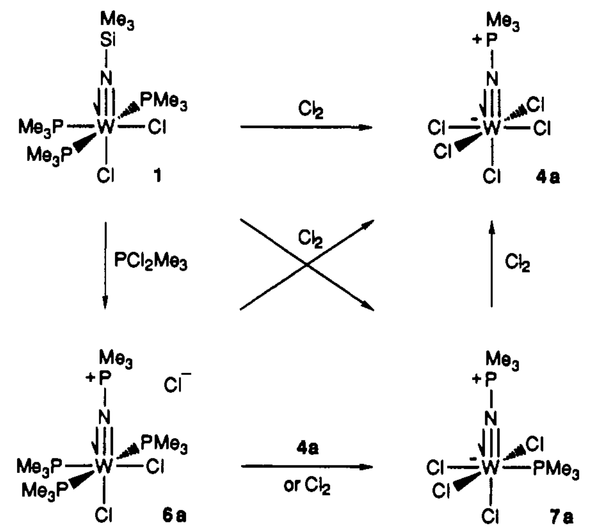


Figure 3. ORTEP drawing of $[W(NPMePh_2)Cl_2(PMe_3)_3]^+$ from **6b**·2MeCN with 50% probability thermal ellipsoids for non-hydrogen atoms.

Scheme II



(1.628 (3) Å for **6a** and 1.630 (4) Å for **6b**) somewhat shorter than those in **4a** and W–N bonds (1.789 (3) Å for **6a** and 1.791 (4) Å for **6b**) just outside the range observed for triply-bonded imido complexes. These bond distances suggest that contributions from the double-bonded resonance structure, $[(Me_3P)_3Cl_2W{=}N{=}PR_3]^+$, may be important in describing **6**. Nonetheless, the diamagnetic character of these d^2 complexes suggests that the resonance structure $[(Me_3P)_3Cl_2W{\equiv}N{-}PR_3]^+$ is also an important contributor. Formation of a metal–nitrogen triple bond (taken as the z-axis) destabilizes the d_{xz} and d_{yz} orbitals, which comprise a pair of metal–nitrogen π-antibonding orbitals. This places the pair of d-electrons in the nonbonding d_{xy} orbital perpendicular to the metal–nitrogen bond axis, resulting in a diamagnetic complex with an electronic structure analogous to that of the closely related tungsten(IV) imido complexes, $(R_3P)_3Cl_2W{\equiv}N{-}R$.[3,24]

Compounds **6a–c** react rapidly with excess chlorine in dichloromethane to produce the tungsten(VI) phosphoraniminato complexes **4a,b** and $W(NPPh_3)Cl_5$ (**4c**) (eq 3). This contrasts

$$\underset{\mathbf{6a-c}}{[W(NPR_3)Cl_2(PMe_3)_3]Cl} + \text{excess } Cl_2 \rightarrow \underset{\mathbf{4a-c}}{W(NPR_3)Cl_5} \quad (3)$$

with previous observations in an osmium phosphoraniminato system in which chlorinations of $Os(NPR_3)Cl_3(PR_3)_2$ produce nitrido complexes $Os(N)Cl_3(PR_3)_2$ in good yield.[25] The reactions of **6b** and **6c** with Cl_2 initially produce predominantly **4b** and **4c**, respectively. A small amount of **4a** is also observed in the initial spectra for the reaction mixtures, and this species grows in over time, suggesting that its origin is the PCl_2Me_3 byproduct of reaction 3. Consistent with this we have independently demonstrated that **6b** and **6c** react with PCl_2Me_3 in dichloromethane to exchange P^VMe_3 for the phosphoraniminato P^VR_3 group (eq 4). Thus, the

$$\underset{\mathbf{4b,c}}{W(NPR_3)Cl_5} \xrightarrow[-PCl_2R_3]{+PCl_2Me_3} \underset{\mathbf{4a}}{W(NPMe_3)Cl_5} \quad (4)$$

reactions of **6b** and **6c** with Cl_2 occur at the metal center and the coordinated PMe_3 ligands, leaving the phosphoraniminato PR_3 group intact in the initially formed $W(NPR_3)Cl_5$ products (**4b,c**).

Formation of a Tungsten(V) Phosphoraniminato Complex. In addition to the tungsten(IV) and -(VI) phosphoraniminato complexes described above, a tungsten(V) phosphoraniminato complex has also been characterized in this system. $W(NPMe_3)Cl_4(PMe_3)$ (**7a**) is formed in the reaction of either $W(NSiMe_3)Cl_2(PMe_3)_3$ (**1**) or $[W(NPMe_3)Cl_2(PMe_3)_3]Cl$ (**6a**) with a limited amount of chlorine in dichloromethane (Scheme II). Compound **7a** can be isolated in good yield from this reaction along with a small amount of **4a**. Subsequent further addition of Cl_2 converts **7a** to **4a** in nearly quantitative yield (Scheme II). Alternatively, **7a** can be prepared by the conproportionation of **4a** and **6a** in dichloromethane and is isolated in high yield as a green crystalline solid from this reaction (eq 5). According to the stoichiometry

$$\underset{\mathbf{4a}}{W(NPMe_3)Cl_5} + \underset{\mathbf{6a}}{[W(NPMe_3)Cl_2(PMe_3)_3]Cl} \rightarrow \underset{\mathbf{7a}}{2W(NPMe_3)Cl_4(PMe_3)} \quad (5)$$

of this reaction, 1 equiv of PMe_3 should be eliminated; however, free PMe_3 is not observed due to its rapid reaction reducing **4a**. This prevents quantitative formation of **7a** by reaction 5. Elemental analysis confirms the empirical composition of **7a**, and its infrared spectrum contains a very strong vibration at 1173 cm^{-1} assigned to ν_{WNP}. (^1H and ^{31}P NMR spectroscopy are not of use in characterizing this d^1 complex.) An X-ray diffraction study of the bis(acetonitrile) solvate of **7a** indicates an octahedral structure with coordination of the phosphine ligand cis to the phosphoraniminato (Figure 4). The distances and angles for **7a** are comparable to those for **4a**, **6a**, and **6b** (Table I), suggesting an analogous description of the WNP bonding.

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[24] Su, F.-M.; Bryan, J. C.; Jang, S.; Mayer, J. M. *Polyhedron*, **1989**, *8*, 1261–1277 and references therein.

[25] Pawson, D.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1975**, 417–423.

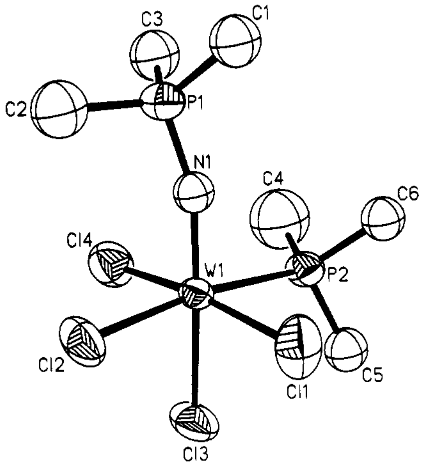

Figure 4. ORTEP drawing of $W(NPMe_3)Cl_4(PMe_3)$ from **7a**·2MeCN with 50% probability thermal ellipsoids for non-hydrogen atoms.

The series of reactions described for the tungsten/PMe_3 system are summarized in Scheme II and suggest that **6a** and/or **7a** may be intermediates in the formation of **4a** from **1** plus chlorine. We are currently exploring this question.[26]

Reactions of Molybdenum(IV) Silylimido Complexes with PCl_2R_3. The known[12] molybdenum(IV) phosphoraniminato compound $[Mo(NPMe_3)Cl_2(PMe_3)_3]Cl$ (**8a**) is readily formed by the reaction of **2** with PCl_2Me_3 in dichloromethane (eq 6).

$$\underset{\mathbf{2}}{Mo(NSiMe_3)Cl_2(PMe_3)_3} + PCl_2R_3 \xrightarrow{-ClSiMe_3} \underset{\mathbf{8}}{[Mo(NPR_3)Cl_2(PMe_3)_3]Cl} \xrightarrow{-PR_3} \tfrac{1}{2}[Mo_2(N)Cl_6(PMe_3)_4][Me_3PNPMe_3] \qquad (6)$$

Gibson and co-workers have reported the structure of **8a** and its slow conversion into the dimolybdenum nitride-bridged compound $[Mo_2(N)Cl_6(PMe_3)_4][Me_3PNPMe_3]$ over several days at room temperature in dichloromethane solution.[12] The molybdenum(IV) methyldiphenyl- and triphenylphosphoraniminato compounds $[Mo(NPMePh_2)Cl_2(PMe_3)_3]Cl$ (**8b**) and $[Mo(NPPh_3)Cl_2(PMe_3)_3]Cl$ (**8c**) are also generated from **2** plus PCl_2MePh_2 and PCl_2Ph_3 (eq 6) according to the ^1H and ^{31}P NMR spectra of these green reaction mixtures. However, these compounds undergo subsequent conversion to orange nitride-bridged products (eq 6) much more rapidly than **8a**, precluding generation of pure samples of **8b** or **8c**. Surprisingly, however, all three phosphoraniminato compounds produce $[Mo_2(N)Cl_6(PMe_3)_4]^-$ with $[Me_3PNPMe_3]^+$ as the counterion according to X-ray diffraction data and IR spectroscopy of the solids isolated from reaction 6. Additionally, free $PMePh_2$ and free PPh_3 are detected by NMR spectroscopy in the reactions of **8b** and **8c**, respectively. The pathway for formation of $[Mo_2(N)Cl_6(PMe_3)_4][Me_3PNPMe_3]$ from **8b** and **8c** is not known. However, isolation of the nitride-bridged species as $[Me_3PNPMe_3]^+$ salts is not surprising because we have independently demonstrated that bis(organophosphine)nitrogen(1+) cations undergo fast reaction with free trimethylphosphine to exchange PR_3 groups (eq 7) under conditions comparable to those of reaction 6.

$$[Ph_3PNPPh_3]Cl + PMe_3 \rightarrow [Me_3PNPMe_3]Cl + PPh_3 \qquad (7)$$

Other Routes to Phosphoraniminato Complexes and Synthesis of a Nitride-Bridged Tungsten Complex. Attack of free phosphine on transition-metal nitrido ligands is usually a general route to phosphoraniminato complexes.[6,19] For example, as reported by Gibson and co-workers, $[Mo(NPMe_3)Cl_2(PMe_3)_3]Cl$ (**8a**) is produced in good yield by the reaction of $Mo(N)Cl_3$ with trimethylphosphine in dichloromethane.[12] However, the analogous tungsten reaction produces **6a** in less than 50% yield, and no reaction is observed between $W(N)Cl_3$ and $PMePh_2$ or PPh_3 in dichloromethane at room temperature.[27] In contrast, reaction of the tungsten nitride with PCl_2Ph_3 provides a route to **4c** (eq 8). The reaction is very slow, requiring days at room temperature,

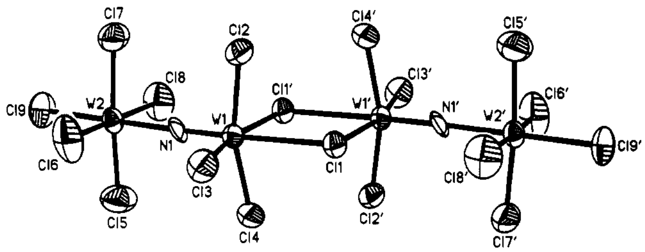

Figure 5. ORTEP drawing of $[W_2(N)Cl_9]_2^{2-}$ from **10** with 50% probability thermal ellipsoids.

$$W(N)Cl_3 + PCl_2R_3 \rightarrow W(NPR_3)Cl_5 \qquad (8)$$
$$PR_3 = PPh_3, \mathbf{4c}$$

which may be a function of the poor solubility of the tungsten nitride in the dichloromethane solvent.

The tungsten(VI) triphenylphosphoraniminato complex $W(NPPh_3)Cl_5$ (**4c**) is most readily prepared by the reaction of WCl_6 with 1 equiv of $Me_3SiNPPh_3$ in dichloromethane (eq 9).[11] Addition of a second equiv of $Me_3SiNPPh_3$ to $W(NPPh_3)Cl_5$ (**4c**) produces the yellow tungsten(VI) bis(triphenylphosphoraniminato) complex $W(NPPh_3)_2Cl_4$ (**9c**) (eq 10).[11] Similarly, a mixed bis(phosphoraniminato)tungsten(VI) complex, $W(NPPh_3)(NPMePh_2)Cl_4$ (**9b**), can be prepared from **4c** plus $Me_3SiNPMePh_2$ (eq 10). The d^0 electron count suggests a cis

$$WCl_6 + Me_3SiNPPh_3 \xrightarrow{-ClSiMe_3} \underset{\mathbf{4c}}{W(NPPh_3)Cl_5} \qquad (9)$$

$$\begin{array}{lcl} W(NPPh_3)Cl_5 + Me_3SiNPR_3 & \xrightarrow{-ClSiMe_3} & W(NPPh_3)(NPR_3)Cl_4 \\ \mathbf{4c} \quad PR_3 = PMePh_2 & & \mathbf{9b} \\ \mathbf{4c} \quad PR_3 = PPh_3 & & \mathbf{9c} \end{array} \qquad (10)$$

structure for these complexes, analogous to that observed for two structurally characterized bis(phosphoraniminato)tungsten(VI) fluorides, $W(NPMe_3)_2F_4$ and $W(NPPh_3)_2F_4$.[28] Surprisingly, the trimethylphosphoraniminato analogue of **9** is not readily prepared by either the reaction of **4c** with $Me_3SiNPMe_3$ or the reaction of **4a** with $Me_3NSiPPh_3$. Instead, complex mixtures of products are obtained from both these reactions.

In contrast to the high-yield formation of **4c** from tungsten hexachloride plus $Me_3SiNPPh_3$, reaction of WCl_6 with $Me_3SiNPMePh_2$ in dichloromethane solution produces a reduced nitride-bridged compound, $[W_2(N)Cl_9]_2[PClMePh_2]_2$ (**10**) (eq 11), highlighting the significance of the P^VR_3 group in determining the reactivity in this system. This black crystalline solid, which is readily soluble in coordinating organic solvents, is isolated from this reaction in greater than 80% yield. Elemental analysis confirms the empirical composition of **10**, and an X-ray diffraction study (Figure 5) shows it to be an ionic compound containing a dichloro-bridged dimer of a nitride-bridged ditungsten anion (III), with a short W-N triple bond (1.682 (10) Å), a longer W-N single bond (2.050 (10) Å), and an almost linear WNW angle (177.6 (6)°). The expected distortions[21b] from idealized octahedral

$$WCl_6 + Me_3SiNPMePh_2 \rightarrow \underset{\mathbf{10}}{[W_2(N)Cl_9]_2[PClMePh_2]_2} \qquad (11)$$

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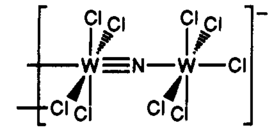
(26) DeCoster, D. M.; Doherty, N. M. Work in progress.

(27) Reactions of $Mo(N)Cl_3$ and $W(N)Cl_3$ with PPh_3 in boiling dichloromethane have previously been reported to yield $Mo(NPPh_3)Cl_3$ and $W(NPPh_3)Cl_3$. Kolitsch, W.; Dehnicke, K. *Z. Naturforsch.* **1970**, *25B*, 1080–1082. Schmidt, I.; Kynast, U.; Hanich, J.; Dehnicke, K. *Z. Naturforsch.* **1984**, *39B*, 1248–1251.

(28) Roesky, H. W.; Seseke, U.; Noltemeyer, M.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1986**, 1309–1310. Roesky, H. W.; Katti, K. V.; Seseke, U.; Scholz, U.; Herbst, R.; Egert, E.; Sheldrick, G. M. *Z. Naturforsch.* **1986**, *41B*, 1509–1512.



III

geometry are observed at the triply-bonded tungsten atom (W(1) in Figure 5), with the cis chlorides bent away from the nitride ligand and an elongated trans bridging chloride to tungsten distance (W(1)–Cl(1) in Figure 5).

On the basis of its formula, $[W_2(N)Cl_9]^-$ (III) is a d^1 species, formally containing tungsten(VI) and tungsten(V) centers. The solid-state structure, d-electron count, and charge suggest that this species is best described as an adduct in which an anionic tungsten(VI) nitride, $[W(N)Cl_4]^-$, is coordinated via a bridging nitrido ligand to a neutral tungsten(V) chloride fragment, WCl_5. An analogous formulation has previously been reported for the closely related mixed-valence nitride-bridged molybdenum compound $[Mo_2(N)Cl_9]_2[PPh_4]_2$.[29] Structural characterization of this species has shown that it contains a dichloro-bridged dimer of a nitride-bridged dimolybdenum anion analogous to III, and synthetic studies indicate that it can be prepared in excellent yield from the reaction of $[MoNCl_4][PPh_4]$ with $MoCl_5$.[29] In contrast, it is not clear why **10** forms in such good yield in reaction 11 nor is it clear how **10** is produced. Reactions of $W(NPR_3)Cl_5$ (**4**) with WCl_6 do not yield **10** or its analogues, ruling out this simple route to such compounds. One other mixed-valence tungsten(V/VI) dimetallonitride, $[W_2(N)Cl_{10}][AsPh_4]_2$, is known.[30] As for **10**, the details involved in its high-yield synthesis (by decomposition of $[WNCl_4][AsPh_4]$) are not understood.

Summary and Conclusions

Molybdenum and tungsten phosphoraniminato complexes are readily prepared from the metal(IV) silylimido complexes, $M(NSiMe_3)Cl_2(PMe_3)_3$. Reactions with chlorine produce metal(V) and metal(VI) phosphoraniminato complexes, depending on the number of equivalents of oxidant added, while additions of organophosphine dichlorides yield the metal(IV) phosphoraniminato compounds. The facility of the latter reaction, which can be considered a main-group analogue of the condensation reaction used to form nitrido-bridged metal complexes, suggests that addition of PCl_2R_3 to $L_nM(NSiMe_3)$ may be a useful general route to phosphoraniminato complexes.

Nitrido-bridged complexes, formed either by decomposition of phosphoraniminato species or in attempts to develop alternative syntheses of phosphoraniminato species, have additionally been observed in the molybdenum and tungsten systems described here. These suggest the potential for use of phosphoraniminato complexes as alternative precursors for the synthesis of nitride-bridged transition-metal compounds and materials, an area we are currently exploring.

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Supplementary Material Available: Tables of X-ray diffraction data for **4a**, **6a**·toluene, **6b**·2MeCN, **7a**·2MeCN, and **10**, including structure determination summaries, atomic coordinates, interatomic distances, interatomic angles, anisotropic displacement coefficients, and hydrogen atom coordinates and additional ORTEP drawings (42 pages); tables of observed and calculated structure factors (75 pages). Ordering information is given on any current masthead page.

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Contribution from the CNR Centro di Studio sulla Sintesi e la Struttura dei Composti dei
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Mixed Rhodium–Osmium Carbonyl Clusters. Synthesis of the Anions $[OsRh_5(CO)_{16}]^-$ and $[OsRh_3(CO)_{12}]^-$ and Crystal Structures of Their (μ-Nitrido)bis(triphenylphosphorus)(1+) Salts

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The two new anions $[OsRh_5(CO)_{16}]^-$ (**1**) and $[OsRh_3(CO)_{12}]^-$ (**2**) have been obtained, in a 1:1 mixture, by acidification of $[OsRh_4(CO)_{15}]^{2-}$. Alternative synthetic routes have been devised: **1** may be also produced by condensation of Rh^I derivatives on $[OsRh_4(CO)_{15}]^{2-}$ or, more conveniently, with a one-pot synthesis, starting from $Os_3(CO)_{12}$ and $Rh_4(CO)_{12}$; **2** may be obtained by oxidative demolition of $[OsRh_4(CO)_{15}]^{2-}$ with iodine. Both anions were characterized by single-crystal X-ray diffraction of their $[(Ph_3P)_2N]^+$ (PPN) salts. (PPN)$[OsRh_5(CO)_{16}]$: space group $C2/c$, $Z = 8$, $a = 33.665$ (4) Å, $b = 9.752$ (1) Å, $c = 33.785$ (5) Å, $\beta = 94.45$ (1)°, $R = 0.030$, and $R_w = 0.031$ for 5166 independent reflections with $I > 3\sigma(I)$. (PPN)$[OsRh_3(CO)_{12}]$: space group $P2_1/c$, $Z = 4$, $a = 14.707$ (3) Å, $b = 21.371$ (6) Å, $c = 16.095$ (3) Å, $\beta = 102.83$ (2)°, $R = 0.037$, and $R_w = 0.037$ for 3007 independent reflections with $I > 3\sigma(I)$. Anion **1** shows a $Rh_6(CO)_{16}$-like structure with 12 terminal carbonyls (2 on each metal) and 4 triply bridging on the alternate faces of the octahedral skeleton. Anion **2** has a tetrahedral metal frame with an unprecedented ligand disposition, 7 terminal and 5 bridging carbonyls with overall C_s ideal symmetry. ^{13}C NMR spectra in the temperature range 323–183 K evidenced a fluxional behavior in **2**, from complete CO scrambling to a static situation consistent with the solid-state structure; compound **1** was found to be static at room temperature.

Introduction

Our previous investigations on the Os–Rh bimetallic system led to the synthesis and characterization of $[OsRh_4(CO)_{15}]^{2-}$,[2] a product which can be obtained as the $[(Ph_3P)_2N]^+$ (PPN) salt on a several hundred milligrams scale and is therefore a suitable starting material. The study of its reactivity yielded two new species, the anions $[OsRh_5(CO)_{16}]^-$ and $[OsRh_3(CO)_{12}]^-$, here

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[2] Fumagalli, A.; Garlaschelli, L.; Della Pergola, R. *J. Organomet. Chem.* **1989**, *362*, 197.

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