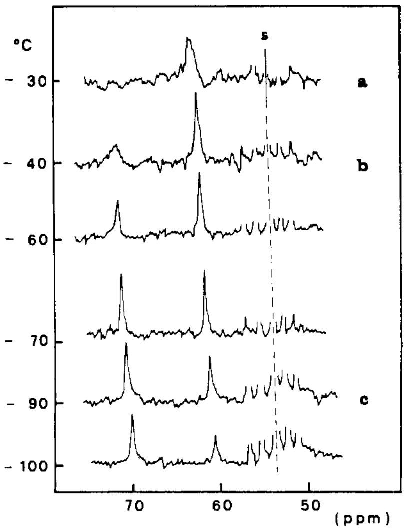

Figure 4. Temperature-dependent 20-MHz ^{13}C spectra for carbon atom CH(c) of **2** in $CHClF_2/CD_2Cl_2$ (3:1 v/v) at (a) −30 °C (near coalescence), (b) −40 °C (slow-exchange limit), and (c) −90 °C (inversion of conformer/conformer ratio).

a new small signal appearing to its left. Analysis is complex because the exchange is over three sites, and the exchange shows variation of population with temperature.

Our interpretation of the phenomenon is that at room temperature there is an averaged signal coming from the exchange between the three sites $RR(\delta\delta)$, stepped $RR(\delta\lambda)$, and umbrella $RR(\lambda\lambda)$, with the equilibrium strongly shifted toward an umbrella form. At −40 °C we have the separation of the two diastereoisomers umbrella $RR(\delta\delta)$ and umbrella $RR(\lambda\lambda)$: two signals rise by these two diastereoisomers in slow equilibrium. The signals are of different intensity, showing the existence of a prevailing umbrella conformation, in agreement with the results of previous CD studies.[3c] As far as the stepped form is concerned, separate signals of equal intensity between the lines corresponding to the two umbrella forms are not observed in the ^{13}C NMR spectrum. Possibly, there may be a signal of the "stepped" conformer under each "umbrella" line.

A molar fraction of 0.94 of the $RR(\delta\delta)$ umbrella form is calculated[12] because the stepped form, if present, would contribute one signal under each peak of the umbrella form in equal intensity. The prevalence of this diastereoisomer should increase at lower temperature. On the contrary, an inversion of the population ratio is observed upon further lowering the temperature (Figure 4). This inversion is observed only with $CHClF_2$ while CCl_3F, $CHCl_2F$, or a mixture of them does not give this inversion. Several authors[13] have reported a marked solute–solvent interaction in experiments with fluorinated solvents, in particular when there is a group like *tert*-butyl, which may account for our observations.

Registry No. **1**, 56647-30-4; **2**, 98574-19-7.

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Contribution from the Departamento de Química Inorgânica, Facultad de Química, Universidad de Sevilla, 41012 Sevilla, Spain, and Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115

Synthesis and Properties of *cis*-Bis(dinitrogen)tetrakis(trimethylphosphine)tungsten(0). Crystal and Molecular Structures of $[W(N_2)(PMe_3)_5]$ and *trans*-$[W(C_2H_4)_2(PMe_3)_4]$

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The dispersed-sodium reduction of $WCl_4(PMe_3)_3$ in tetrahydrofuran under nitrogen gives *cis*-$[W(N_2)_2(PMe_3)_4]$ (**1**), which upon reaction with PMe_3 under argon, at 40–50 °C, affords $[W(N_2)(PMe_3)_5]$ (**2**). If $WCl_4(PMe_3)_3$ is reduced with sodium amalgam in ethylene-saturated tetrahydrofuran, *trans*-$[W(C_2H_4)_2(PMe_3)_4]$ (**3**) is formed. Complex **3** can also be obtained by reaction of **1** with C_2H_4 under UV light. Reaction of **3** with CO (1 atm) yields *trans,mer*-$[W(C_2H_4)_2(CO)(PMe_3)_3]$ (**4**), while with 2–3 atm of CO *trans,trans,trans*-$[W(C_2H_4)_2(CO)_2(PMe_3)_2]$ (**5**) is obtained. The molybdenum analogue of the latter complex, *trans,trans,trans*-$[Mo(C_2H_4)_2(CO)_2(PMe_3)_2]$ (**6**), has been similarly prepared. Compounds **2** and **3** have been studied by X-ray crystallography and found to be isostructural with their corresponding molybdenum analogues. $[W(N_2)(PMe_3)_5]$ (**2**) is orthorhombic, *Pnma*, with unit cell constants $a = 21.990$ (6) Å, $b = 12.108$ (3) Å, $c = 9.722$ (2) Å, and $D_{calcd} = 1.52$ g cm^{-3} for $Z = 4$. **2** was refined to a conventional R value of 0.041 by using 1753 independent observed reflections. The tungsten atom resides on a crystallographic mirror plane, and a W–N bond length of 2.04 (2) Å is observed. *trans*-$[W(C_2H_4)_2(PMe_3)_4]$ (**3**) crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.130$ (3) Å, $b = 13.699$ (4) Å, $c = 17.029$ (6) Å, $\beta = 98.84$ (2)°, and $D_{calcd} = 1.53$ g cm^{-3} for $Z = 4$. The final R value based on 1465 reflections is 0.028. The two ethylene groups are trans and mutually perpendicular. The average W–C and W–P bond separations are 2.26 (1) and 2.48 (1) Å, respectively.

Introduction

The chemistry of dinitrogen complexes of molybdenum and tungsten continues to attract much attention and to produce new and exciting results. Although much of the activity in this area is devoted to studies related to mimicking the function of nitrogenase,[2] a great deal of effort has been dedicated to the search for novel types of complexes and modes of dinitrogen coordination and to the study of the new reaction chemistry of these interesting species. The recent characterization of a tungsten–aluminum complex[3] containing a triply end-on-bridged dinitrogen ligand, the synthesis and structural determination of the tris(dinitrogen) complex *mer*-$[Mo(N_2)_3(P\text{-}n\text{-}Pr_2Ph)_3]$,[4] and the formation of η^6-pyridine[5] and bis(carbon dioxide)[6] derivatives of molybdenum(0) may be noted among the many significant contributions reported in this field in the last few years.

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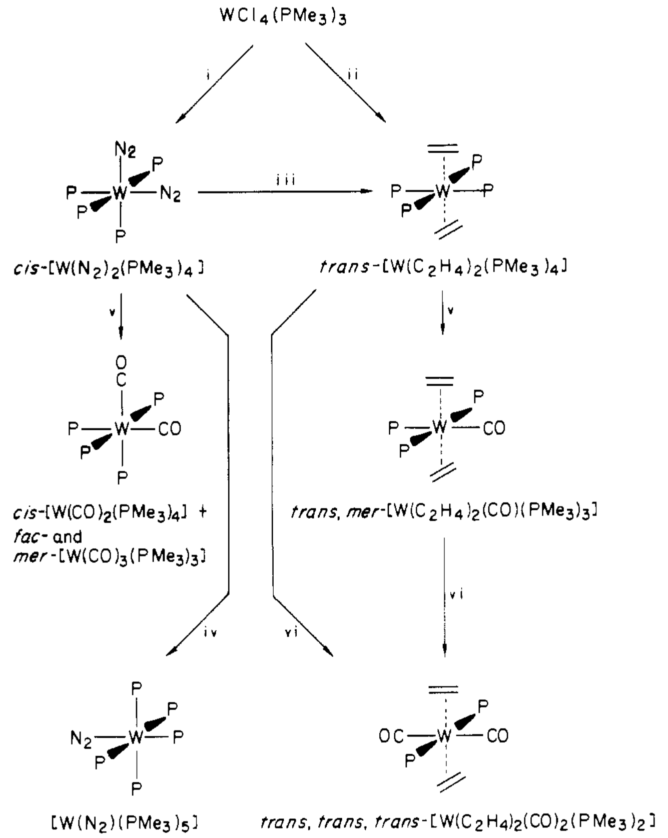
Scheme I[a]



[a] (i) Na, N_2, PMe_3, THF; (ii) Na(Hg), C_2H_4, PMe_3, THF; (iii) C_2H_4 (2 atm), 1 h; (iv) PMe_3, Ar, 40–50 °C; (v) CO (1 atm); (vi) CO (3 atm), 3 days.

In a recent publication we have dealt with the synthesis and properties of some dinitrogen and ethylene trimethylphosphine complexes of molybdenum.[7] We have extended this work to the tungsten analogues,[8] and here we report the preparation of *cis*-$[W(N_2)_2(PMe_3)_4]$ (**1**) and *trans*-$[W(C_2H_4)_2(PMe_3)_4]$ (**3**) by the one-flask reduction of $WCl_4(PMe_3)_3$ under appropriate conditions. An account of some of the chemical properties of these compounds (Scheme I) is also reported, particularly the conversion of **1** into $[W(N_2)(PMe_3)_5]$ (**2**) by interaction with PMe_3 under argon at 40–50 °C and the stepwise formation of the carbonyl complexes *trans,mer*-$[W(C_2H_4)_2(CO)(PMe_3)_3]$ (**4**) and *trans,trans,trans*-$[W(C_2H_4)_2(CO)_2(PMe_3)_2]$ (**5**) by reaction of **3** with carbon monoxide. Previously unknown *trans,trans,trans*-$[Mo(C_2H_4)_2(CO)_2(PMe_3)_2]$ (**6**) has been synthesized by a similar procedure, and its properties have been described. The crystal and molecular structures of complexes **2** and **3** are also discussed. Part of this work has been reported in preliminary form.[8]

Results and Discussion

Synthesis and Properties of *cis*-$[W(N_2)_2(PMe_3)_4]$ (1). Sodium reduction of WCl_4 or WCl_4L_x (L = tertiary phosphine; x = 2, 3) is known to yield[9,10] several mononuclear or binuclear complexes of tungsten in lower oxidation states, including the important species $W_2Cl_4L_4$ containing a tungsten–tungsten quadruple bond.[10] In no case however, has reduction all the way to tungsten(0) been observed. Recent work from our laboratory has afforded dinitrogen complexes of molybdenum of the type *cis*-$[Mo(N_2)_2(PMe_3)_4]$ and $[Mo(N_2)(PMe_3)_5]$, by reduction of higher oxidation state molybdenum complexes.[7,11] We set out to prepare the tungsten analogues using $WCl_4(PMe_3)_3$[9,12] as starting material. Although the known complexes $WCl_3(PMe_3)_3$ and $WCl_2(PMe_3)_4$ are obtained as products of its reduction, as described by Schrock and Sharp,[9] under certain conditions reduction to W(0) with formation of the dinitrogen complex **1** takes place as shown in eq 1. The addition of solid $WCl_4(PMe_3)_3$ to a vigorously stirred

$$\mathrm{WCl_4(PMe_3)_3} \xrightarrow[\text{THF}]{\text{Na dispersion, N}_2\text{, PMe}_3} \underset{\mathbf{1}}{cis\text{-}[\mathrm{W(N_2)_2(PMe_3)_4}]} \qquad (1)$$

suspension of sodium in tetrahydrofuran initially produces a brown solution of $WCl_3(PMe_3)_3$. The color of the solution changes slowly to deep green, and after being stirred at room temperature for ca. 40–50 min it darkens to become dark red-brown when the reaction is complete. As found for the molybdenum system,[7] the yield of the reaction improves by addition of 0.7–0.8 equiv of PMe_3 when the green color darkens. Workup of the final dark red-brown solution is considerably facilitated by stirring for 7–8 h, under 3–4 atm of N_2 with indirect exposure to sunlight. After several purification operations, complex **1** can be isolated as a crystalline material.

When pure, complex **1** is a yellow-orange crystalline solid, very soluble in nonpolar solvents and very air sensitive, decomposing immediately upon exposure to air. The cis distribution of the dinitrogen ligands is indicated by the presence of two strong IR absorptions at 1980 and 1920 cm^{-1} (Nujol) and by the observation of two ^1H NMR signals of approximately the same relative intensities at δ 1.5 (pseudotriplet) and 1.3 (doublet with central intensity). Also the ^{31}P NMR spectrum may be interpreted in terms of an A_2X_2 system ($\delta(P_A)$ −34.4, $\delta(P_X)$ −36.5, $^2J(P_A{-}P_X)$ = 7.6 Hz). Coupling to tungsten is also observed with $^1J(W{-}P_A)$ = 314 Hz and $^1J(W{-}P_X)$ = 312 Hz. These coupling constants are similar to those found for related complexes.[13] A well-known empiricism regarding the chemical shift of coordinated tertiary phosphines becomes apparent when a comparison of $\delta(P_A)$ and $\delta(P_X)$ in the complexes *cis*-$[M(N_2)_2(PMe_3)_4]$ (M = Cr,[14] Mo,[7] W) is made. In related compounds of the same coordination number, molecular geometry, oxidation state, and phosphine ligands, a high-field shift of the ^{31}P resonance is observed upon descending in a given group.[15] Not only is this trend clearly followed by the above complexes but furthermore a plot of the atomic number vs. $\delta(P)$ shows an excellent linear correlation for both the low-field and the high-field resonances (Cr 13.8, 9.4; Mo −4.8, −6.9; W −34.4, −36.5 ppm).

Substitution Reactions of *cis*-$[W(N_2)_2(PMe_3)_4]$ (1). X-ray Structure of $[W(N_2)(PMe_3)_5]$ (2). Complex **1** displays an interesting chemistry, similar to that found for the molybdenum analogue,[7] although as it is generally found in related systems[16] the reactions of the tungsten complex are usually slower and frequently require thermal activation or photoactivation. The interaction of **1** with ethylene, CO, and PMe_3 (Scheme I) has been studied and will be discussed in this paper. Other interesting reactions, such as those with protonic acids, carbon dioxide, isonitriles, etc., are presently being investigated and will be reported in subsequent publications.

The reaction of **1** with ethylene is very slow under ambient conditions and provides *trans*-$[W(C_2H_4)_2(PMe_3)_4]$ (**3**) in very low

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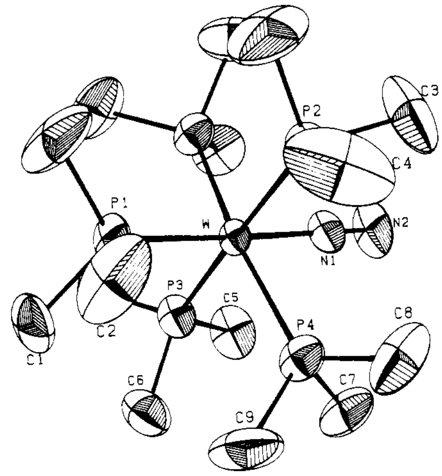

Figure 1. Molecular structure and atom-labeling scheme for [$W(N_2)(PMe_3)_5$] (**2**). The atoms are represented by their 50% probability ellipsoids for thermal motion.

yields together with small amounts of an insoluble unidentified material. Most of the initial dinitrogen compound remains unchanged after stirring at room temperature for ca. 8 h in ethylene-saturated tetrahydrofuran. Obviously, **3** should be best prepared by a different route (vide infra). Conversion of **1** into **3** is not greatly facilitated by carrying out the reaction at 40–50 °C under pressure (2–3 atm of C_2H_4), although irradiation with a tungsten filament lamp induces conversion into **3** at room temperature over a period of ca. 12 h.

Petroleum ether solutions of **1** react with CO at room temperature and pressure with initial substitution of the coordinated N_2 molecules by CO and formation of *cis*-[$W(CO)_2(PMe_3)_4$].[17] Long reaction periods (several hours) cause partial substitution of the phosphine ligands and formation of a mixture of carbonyl complexes. Similar results are obtained if the reaction is carried out under 2–3 atm of CO, and in all cases, some unreacted **1** can be recovered on workup. This contrasts with the behavior found for the Cr and Mo analogues,[7,14] which react quickly with CO with complete substitution of the dinitrogen ligands.

The reaction of **1** with PMe_3 under argon is very slow at room temperature and requires stirring at 40–50 °C for ca. 24 h for completion (eq 2). From the reaction mixture, **2** can be isolated

$$\underset{\mathbf{1}}{cis\text{-}[W(N_2)_2(PMe_3)_4]} + PMe_3 \xrightarrow[40\text{-}50\ ^\circ C]{Ar} \underset{\mathbf{2}}{[W(N_2)(PMe_3)_5]} + N_2 \qquad (2)$$

in very high yield as a yellow, air- and moisture-sensitive crystalline material. Solubility and other properties are very similar to those reported for [$Mo(N_2)(PMe_3)_5$].[7] The IR spectrum of **2** shows, as expected, a single strong absorption at 1905 cm^{-1} (Nujol) due to the N–N stretching of the coordinated dinitrogen molecule. ^1H and ^{31}P NMR data are also in accord with the proposed formation (see Experimental Section).

The molecular structure of complex **2** has been determined by X-ray crystallographic analysis. An ORTEP illustration of **2** is shown in Figure 1. This compound is isostructural with [$Mo(N_2)(PMe_3)_5$].[8] The molecule is essentially octahedral and contains a mirror plane with the tungsten atom, both nitrogen atoms, and P(1), P(2), P(3), C(3), and C(5) in the plane. As in the molybdenum analogue, C(1) was found to be disordered about that mirror plane.

The dinitrogen moiety is bonded to the tungsten atom via a W–N(1) bond distance of 2.04 (2) Å (Table I). This is the same value found for *trans*-[$WCl(N_2)(PMe_3)_4$][18] and [$WH(N_2)_2(dppe)_2$]HCl_2·2THF.[19] This value is also within experimental error of the Mo–N(1) distance of 2.02 (3) Å found for [$Mo(N_2)(PMe_3)_5$].[8] The difference in single-bond metallic radii, Δ_{W-Mo}, is 0.008 Å.[20] The N–N bond length in **2** is 1.11 (2) Å, which compares well with the N–N separations found for [$Mo(N_2)(PMe_3)_5$] (1.12 (3) Å), *trans*-[$Mo(N_2)(dppe)_2$] (1.118 Å),[21] and *trans*-[$Mo(CO)(N_2)(dppe)_2$]·$0.5C_6H_6$ (1.087 Å).[22] The much longer value of 1.19 (3) Å observed in *trans*-[$WCl(N_2)(PMe_3)_4$] was attributed to disorder in that structure.[18]

Table I. Bond Distances (Å) and Angles (deg) for [$W(N_2)(PMe_3)_5$] (**2**)[a]

	Distances		
W–P(1)	2.473 (4)	W–P(2)	2.447 (5)
W–P(3)	2.436 (5)	W–P(4)	2.450 (3)
W–N(1)	2.04 (2)	P(1)–C(1)	1.87 (3)
P(1)–C(2)	1.82 (2)	P(2)–C(3)	1.83 (2)
P(2)–C(4)	1.85 (2)	P(3)–C(5)	1.88 (2)
P(3)–C(6)	1.85 (2)	P(4)–C(7)	1.88 (1)
P(4)–C(8)	1.84 (2)	P(4)–C(9)	1.86 (2)
N(1)–N(2)	1.11 (2)		
	Angles		
P(1)–W–P(2)	89.5 (2)	P(1)–W–P(3)	93.0 (2)
P(2)–W–P(3)	177.4 (2)	P(1)–W–P(4)	96.48 (7)
P(2)–W–P(4)	92.0 (1)	P(3)–W–P(4)	87.7 (1)
P(4)–W–P(4)′	166.5 (1)	P(1)–W–N(1)	176.6 (4)
P(2)–W–N(1)	87.0 (4)	P(3)–W–N(1)	90.4 (4)
P(4)–W–N(1)	83.65 (7)	W–P(1)–C(1)	120.4 (9)
W–P(1)–C(2)	119.7 (6)	C(1)–P(1)–C(2)	85 (1)
C(1)′–P(1)–C(2)	109 (1)	W–P(2)–C(3)	116.8 (8)
W–P(2)–C(4)	123.7 (7)	C(3)–P(2)–C(4)	98 (1)
W–P(3)–C(5)	115.2 (7)	W–P(3)–C(6)	123.5 (5)
C(5)–P(3)–C(6)	97.2 (7)	W–P(4)–C(7)	113.9 (5)
W–P(4)–C(8)	122.6 (6)	C(7)–P(4)–C(8)	94.6 (8)
W–P(4)–C(9)	123.2 (6)	C(7)–P(4)–C(9)	98.4 (8)
C(8)–P(4)–C(9)	98.3 (9)	W–N(1)–N(2)	179.7 (9)
C(2)–P(1)–C(2)′	95 (1)	C(4)–P(2)–C(4)′	91 (2)
C(6)–P(3)–C(6)′	94 (1)		

[a] Primed atoms are related to those in Table IV by *x*, 0.5 − *y*, *z*.

As one would expect, the W–P bond trans to the dinitrogen ligand is longer at 2.473 (4) Å than the average of the remaining four W–P distances (2.444 (7) Å). An average of 2.458 (2) Å was observed for the W–P bond lengths in *trans*-[$WCl(N_2)(PMe_3)_4$].[18]

Synthesis, Properties, and X-ray Structure of *trans*-[$W(C_2H_4)_2(PMe_3)_4$] (3). Addition of solid $WCl_4(PMe_3)_3$ to a stirred suspension of sodium amalgam in tetrahydrofuran under ethylene produces, after stirring at room temperature for a few minutes, a brown solution that subsequently becomes gray-green and finally gray. Addition of 0.7–0.8 equiv of PMe_3 approximately 20–30 min after formation of the gray color followed by further stirring at room temperature for 4–6 h produces a reddish suspension from which complex **3** can be isolated (eq 3). Reduction with dispersed

$$WCl_4(PMe_3)_3 \xrightarrow[THF]{Na(Hg),\ C_2H_4,\ PMe_3} \underset{\mathbf{3}}{trans\text{-}[W(C_2H_4)_2(PMe_3)_4]} \qquad (3)$$

sodium under the same conditions provides **3** in lower yields. Complex **3** is an amber crystalline material, very reactive toward oxygen and moisture. While no bands due to the stretching of the C–C double bonds of the ethylene molecules can be found in the IR spectrum, the presence of coordinated ethylene is evidenced by a weak absorption at ca. 3000 cm^{-1} (KBr). ^1H and ^{31}P NMR studies are not very informative since the ^1H NMR consists of a resonance at δ 1.1 (PMe_3) resembling a pseudotriplet and a

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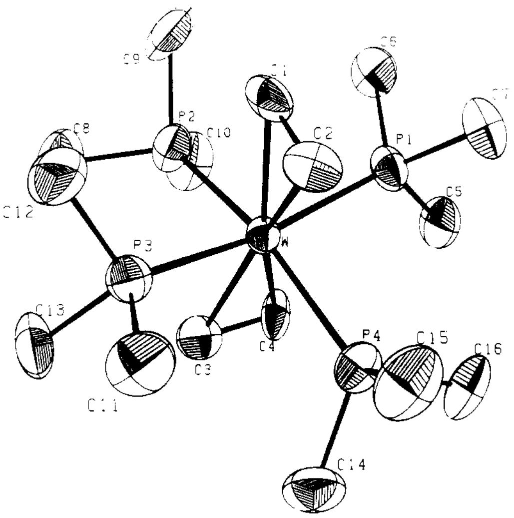


Figure 2. Molecular structure of *trans*-[W$(C_2H_4)_2(PMe_3)_4$] (3).

complex pattern of partially unresolved signals between δ 1.6 and 1.2 (C_2H_4) while the $^{31}P\{^1H\}$ spectrum is a rather broad singlet at δ −36.2 showing tungsten satellites (^1J(W–P) = 239 Hz). The above data suggest a trans configuration of the ethylene ligands, which has been confirmed by an X-ray crystallographic study.

An ORTEP illustration of *trans*-[W$(C_2H_4)_2(PMe_3)_4$] (3) is presented in Figure 2. The complex is essentially octahedral with the ethylene ligands mutually perpendicular, each eclipsing one of the *trans*-P–W–P vectors. This orientation, which is the most favorable,[23,24] was observed for *trans*-[Mo$(C_2H_4)_2(PMe_3)_4$][7] and *trans,mer*-[Mo$(C_2H_4)_2$(CO)$(PMe_3)_3$].[7]

The ethylene moieties are bonded to tungsten at an average W–C separation of 2.26 (1) Å (Table II). The C–C bond lengths average 1.42 (1) Å, which is 0.08 Å larger than that observed in free ethylene. Comparable Mo–C and C–C distances were found for *trans*-[Mo$(C_2H_4)_2(PMe_3)_4$] (2.270 (5), 1.40 (1) Å) and *trans,mer*-[Mo$(C_2H_4)_2$(CO)$(PMe_3)_3$] (2.29 (3), 1.410 (9) Å).

Steric interactions between the phosphine and ethylene ligands are the probable cause of an average W–P bond length of 2.48 (1) Å. This value is longer than the longest W–P separation in [W$(N_2)(PMe_3)_5$] (2.473 (4) Å) but again consistent with *trans*-[Mo$(C_2H_4)_2(PMe_3)_4$] (Mo–P average 2.49 (1) Å).

Reactions of *trans*-[W$(C_2H_4)_2(PMe_3)_4$] (3) with N_2 and CO. Petroleum ether solutions of 3, prepared under N_2, show a medium-intensity IR absorption at 2040 cm^{-1} that is not present when the solutions are prepared under argon or in the presence of added PMe_3. This indicates that one of the phosphine ligands is rather labile and exchanges with N_2, but in contrast to the molybdenum system[7] this process is very slow under ambient conditions. Thus the ^{31}P NMR spectrum of solutions of 3 reacted with N_2 for several hours shows that the *trans*-bis(ethylene) complex is the main species present in solution, although a triplet and a doublet that can be tentatively attributed to *trans,mer*-[W$(C_2H_4)_2(N_2)(PMe_3)_3$] (AX_2 spin system, δ(P_A) −29.1, δ(P_X) −34.4, ^2J(P_A–P_X) = 11 Hz, ^1J(P_A–W) = 281 Hz, ^1J(P_X–W) = 251 Hz) can also be observed. When the above solutions are partially evaporated in vacuo, a bright crystalline solid precipitates that redissolves upon admission of N_2. This sequence can be repeated several times, although partial decomposition takes place and the solution darkens considerably. ^{31}P NMR spectra of solutions of this solid show resonances characteristic of 3 (main species) and of *trans,mer*-[W$(C_2H_4)_2(N_2)(PMe_3)_3$]. It is likely that an equilibrium similar to that found for the molybdenum analogues is set up in solution, although for the tungsten complexes it seems to lie far to the side of 3. Present data are however insufficient to properly characterize this system, particularly to ascertain the nature of the elusive yellow microcrystalline solid that forms upon removal of the solvent in vacuo.

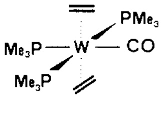
Table II. Bond Distances (Å) and Angles (deg) for *trans*-[W$(C_2H_4)_2(PMe_3)_4$] (3)

	Distances		
W–P(1)	2.472 (3)	W–P(2)	2.477 (3)
W–P(3)	2.499 (3)	W–P(4)	2.477 (3)
W–C(1)	2.24 (1)	W–C(2)	2.27 (1)
W–C(3)	2.26 (1)	W–C(4)	2.25 (1)
P(1)–C(5)	1.84 (1)	P(1)–C(6)	1.85 (1)
P(1)–C(7)	1.82 (1)	P(2)–C(8)	1.83 (1)
P(2)–C(9)	1.83 (2)	P(2)–C(10)	1.84 (1)
P(3)–C(11)	1.81 (1)	P(3)–C(12)	1.84 (1)
P(3)–C(13)	1.81 (1)	P(4)–C(14)	1.84 (1)
P(4)–C(15)	1.84 (1)	P(4)–C(16)	1.85 (1)
C(1)–C(2)	1.42 (2)	C(3)–C(4)	1.41 (2)
	Angles		
P(1)–W–P(2)	91.5 (1)	P(1)–W–P(3)	163.7 (1)
P(2)–W–P(3)	91.8 (1)	P(1)–W–P(4)	90.4 (1)
P(2)–W–P(4)	163.5 (1)	P(3)–W–P(4)	91.0 (1)
P(1)–W–C(1)	79.9 (3)	P(2)–W–C(1)	80.8 (4)
P(3)–W–C(1)	84.8 (3)	P(4)–W–C(1)	115.7 (4)
P(1)–W–C(2)	86.6 (3)	P(2)–W–C(2)	116.6 (4)
P(3)–W–C(2)	77.6 (3)	P(4)–W–C(2)	79.9 (4)
C(1)–W–C(2)	36.6 (4)	P(1)–W–C(3)	116.1 (4)
P(2)–W–C(3)	79.2 (3)	P(3)–W–C(3)	80.3 (4)
P(4)–W–C(3)	85.3 (3)	C(1)–W–C(3)	154.5 (5)
C(2)–W–C(3)	153.0 (5)	P(1)–W–C(4)	80.1 (3)
P(2)–W–C(4)	84.7 (3)	P(3)–W–C(4)	116.2 (3)
P(4)–W–C(4)	79.4 (3)	C(1)–W–C(4)	154.9 (5)
C(2)–W–C(4)	155.2 (4)	C(3)–W–C(4)	36.4 (4)
W–P(1)–C(5)	122.3 (4)	W–P(1)–C(6)	119.0 (4)
C(5)–P(1)–C(6)	95.4 (6)	W–P(1)–C(7)	117.9 (4)
C(5)–P(1)–C(7)	100.9 (6)	C(6)–P(1)–C(7)	96.2 (6)
W–P(2)–C(8)	120.0 (5)	W–P(2)–C(9)	121.6 (5)
C(8)–P(2)–C(9)	96.4 (7)	W–P(2)–C(10)	117.9 (5)
C(8)–P(2)–C(10)	97.4 (7)	C(9)–P(2)–C(10)	98.3 (7)
W–P(3)–C(11)	120.6 (4)	W–P(3)–C(12)	118.3 (5)
C(11)–P(3)–C(12)	96.8 (7)	W–P(3)–C(13)	120.5 (5)
C(11)–P(3)–C(13)	96.0 (7)	C(12)–P(3)–C(13)	99.5 (7)
W–P(4)–C(14)	119.1 (4)	W–P(4)–C(15)	120.7 (5)
C(14)–P(4)–C(15)	98.6 (6)	W–P(4)–C(16)	120.3 (4)
C(14)–P(4)–C(16)	96.0 (6)	C(15)–P(4)–C(16)	96.7 (6)
W–C(1)–C(2)	72.9 (7)	W–C(2)–C(1)	70.5 (7)
W–C(3)–C(4)	71.1 (7)	W–C(4)–C(3)	72.5 (7)

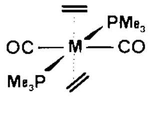
Room-temperature and -pressure carbonylation of 3 produces substitution of one PMe_3 ligand by CO and formation of *trans,mer*-[W$(C_2H_4)_2$(CO)$(PMe_3)_3$] (4) as shown in eq 4. The

$$\underset{\mathbf{3}}{trans\text{-}[W(C_2H_4)_2(PMe_3)_4]} + CO \rightarrow \underset{\mathbf{4}}{trans,mer\text{-}[W(C_2H_4)_2(CO)(PMe_3)_3]} + PMe_3 \quad (4)$$

reaction can be monitored by IR spectroscopy, following the formation of a new strong band at 1860 cm^{-1} due to complex 4. This complex is a colorless crystalline material, very soluble in nonpolar organic solvents. Strong back-donation from the metal to the carbonyl group is indicated by the low value of ν(C=O) at 1860 cm^{-1} (petroleum ether; 1810 cm^{-1}, KBr). A trans,mer configuration, A, is proposed for this compound since the phosphine ligands yield a virtually coupled triplet and a doublet in the ^1H NMR spectrum and an AX_2 pattern of lines in the $^{31}P\{^1H\}$ NMR spectrum. The ^{13}C NMR is also consistent with this arrangement of the ligands in the molecule of A and shows three broad unresolved resonances for the olefinic carbons at δ 27.1, 22.0, and 18.5, of relative intensities ca. 1:1:2, respectively, consistent with restricted rotation around the metal olefin bonds, and



A



B

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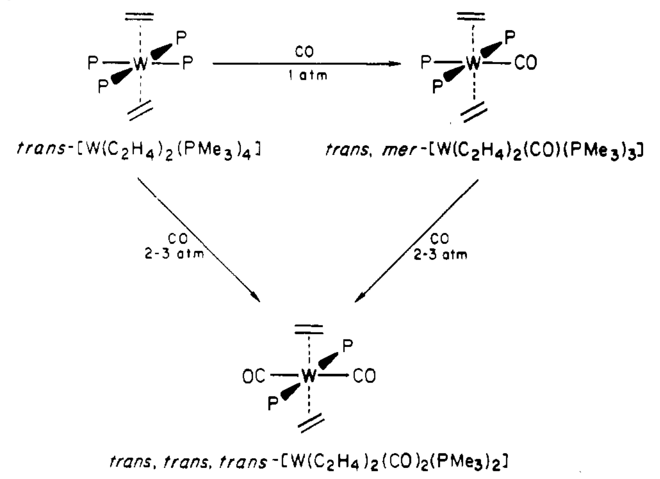
Scheme II



a doublet of triplets centered at δ 217.8 for the carbonyl ligand ($^2J(C-P_{trans})$ = 37.6 Hz, $^2J(C-P_{cis})$ = 7 Hz).

It is interesting to point out that in the analogous, structurally characterized, molybdenum complex, ***trans,mer***-[$Mo(C_2H_4)_2(CO)(PMe_3)_3$], the Mo–P distances for the two trans PMe_3 ligands are considerably shorter than the Mo–P distance trans to CO (2.487 (2) average vs. 2.561 (1) Å). It is likely that this is also the case in complex **4**, since both compounds show similar spectroscopic properties, particularly very close C–O stretching frequencies. The above observation leads to CO being higher than PMe_3 in the trans-influence series for these M(0) complexes. If the same order holds for the trans-effect series, formation of the complexes *trans,trans,trans*-[$M(C_2H_4)_2(CO)_2(PMe_3)_2$] is to be expected upon further carbonylation, and indeed these complexes (M = W (**5**), M = Mo (**6**)) are obtained when the carbonylation reactions are carried out under pressure, as shown in Scheme II.

Compounds **5** and **6** are pale yellow crystalline solids, also very soluble in common organic solvents. Due possibly to solid-state effects, the IR spectra of Nujol mulls of **5** and **6** show broad absorptions for ν(CO) over the range 1950–1700 cm^{-1}. However, in petroleum ether solutions complex **6** displays a strong band at 1840 cm^{-1} together with weaker absorptions at 1950 and 1790 cm^{-1}. On the basis of ^{1}H, ^{13}C, and ^{31}P NMR data (see Experimental Section) a trans,trans,trans configuration, B, can be proposed for these complexes.

Experimental Section

Microanalyses were carried out by Pascher Microanalytical Laboratory, Bonn. Infrared spectra were recorded on a Perkin-Elmer Model 577. ^{1}H NMR spectra were run on a Perkin-Elmer R12A. ^{1}H, ^{31}P, and ^{13}C NMR spectra were run on a Varian XL-200. ^{31}P NMR shifts are referenced to external 85% H_3PO_4.

All preparations and operations were carried out under oxygen-free nitrogen or argon by following the conventional Schlenk techniques. Solvents were dried by standard techniques and degassed before use. The petroleum ether had bp 40–60 °C. The sodium used was purchased from Alfa as a 40% dispersion in mineral oil, and after weighing, it was transferred to the deoxygenated reaction flask and washed with ether (2 × 25 mL) and THF (2 × 25 mL). $WCl_4(PMe_3)_x$[9,12] (x = 2, 3) and PMe_3[25] were prepared by published methods.

Synthesis of *cis*-[$W(N_2)_2(PMe_3)_4$] (1). $WCl_4(PMe_3)_2$ (4.8 g, 10 mmol) was added to a mixture of PMe_3 (1 mL, ca. 10 mmol) and dispersed sodium (excess, ca. 1.6 g) in 100 mL of THF. A red-purple microcrystalline precipitate of $WCl_4(PMe_3)_3$ immediately formed (alternatively, $WCl_4(PMe_3)_3$ can directly be used for the reaction) and was stirred for 60–70 min until conversion into $WCl_3(PMe_3)_3$ was complete. The stirring was continued for another 30–40 min when the color became light green and then dark green. Approximately 20–30 min after the appearance of the green color 0.8 mL (ca. 8 mmol) of PMe_3 was added, and the resulting mixture was stirred overnight under an atmosphere of N_2. A red-brown suspension was obtained and evaporated to dryness, and the residue was extracted with petroleum ether (60 mL) and centrifuged. The solution was decanted, transferred to a pressure bottle, pressurized with 3–4 atm of N_2, and stirred at room temperature for 7–8 h under indirect sunlight. After centrifugation, yellow-orange **1** was crystallized from this solution by partial removal of the solvent in vacuo and cooling at −20 °C overnight. The crude product obtained by evaporation of the above solution is usually pure enough to be used for synthetic purposes without further purification. The yield of the reaction is ca. 45–50% referred to PMe_3. The use of $WCl_3(PMe_3)_3$ as starting material for the synthesis of **1** does not improve the yield any further. IR (hexane): 1980 s, 1920 s cm^{-1} (ν(N≡N)). ^{1}H NMR (C_6H_6): δ 1.3 d, 1.5 pseudotriplet (18 H:18 H). $^{31}P\{^1H\}$ NMR (C_6D_6), A_2X_2 spin system: $\delta(P_A)$ −34.4, $\delta(P_X)$ −36.5, $^2J(P_A-P_X)$ = 7.6 Hz, $^1J(W-P) \simeq$ 313 Hz. Anal. Calcd for $WC_{12}H_{36}N_4P_4$: C, 26.5; H, 6.7; N, 10.3; P, 22.7. Found: C, 26.7; H, 6.7; N, 10.8; P, 21.9.

[$W(N_2)(PMe_3)_5$] (2). Complex **1** (0.54 g, 1 mmol), dissolved in petroleum ether (25 mL), was reacted with an excess of PMe_3 (0.25 mL, ca. 2.5 mmol) under argon at 40–50 °C for 24 h. The resulting solution was evaporated in vacuo and the yellow residue extracted with 25 mL of petroleum ether and centrifuged. Partial evaporation of the solvent and cooling at −20 °C afforded yellow crystals of **2** in 90% yield. IR (hexane): 1905 s cm^{-1} (ν(N≡N)). ^{1}H NMR (C_6H_6): δ 1.7 (br s, 36), 1.4 (d, 9, $^2J(H-P)$ = 5 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6), AX_4 spin system: $\delta(P_A)$ −38.6, $\delta(P_X)$ −36.6, $^2J(P_A-P_X)$ = 9 Hz, $^1J(P_A-W)$ = 303 Hz, $^1J(P_X-W)$ = 295 Hz. Anal. Calcd for $WC_{15}H_{45}N_2P_5$: C, 30.4; H, 7.6; N, 4.7. Found: C, 29.7; H, 7.5; N, 4.6.

***trans*-[$W(C_2H_4)_2(PMe_3)_4$] (3).** PMe_3 (0.8 mL, ca. 8 mmol) and $WCl_4(PMe_3)_2$ (4.1 g, 8 mmol) were successively added in this order to a suspension of Na(Hg) (1%, ca. 0.9 g of Na) in 80 mL of ethylene-saturated THF. Formation of red-purple microcrystals of $WCl_4(PMe_3)_3$ was immediately observed, and this compound was taken into solution and reduced to $WCl_3(PMe_3)_3$ after stirring at room temperature for a few minutes. Further stirring induced a change in color to gray-green and then gray, and ca. 30–40 min later, 0.4 mL (ca. 4 mmol) of PMe_3 was added. The mixture was stirred for 4–5 h at room temperature and centrifuged and the solvent removed under vacuum. The residue was extracted with petroleum ether (50 mL) and centrifuged. Partial removal of the solvent and cooling at −20 °C afforded amber crystals of **3** (2.6 g, 60% yield from this and subsequent crystallizations of the mother liquors). Complex **3** can also be obtained by reaction of **1** with 2–3 atm of C_2H_4 under UV irradiation, albeit in lower overall yields and with longer reaction times. IR (KBr and hexane): 3000 w and 3020 w cm^{-1}, respectively (ν(=C—H)). ^{1}H NMR (C_6H_6): δ 1.1 (br, PMe_3), 1.50, 1.40, 1.25 (m, C_2H_4). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −36.2 (s, $^1J(P-W)$ = 239 Hz). Anal. Calcd for $WC_{16}H_{44}P_4$: C, 35.3; H, 8.1. Found: C, 34.9; H, 8.0.

***trans,mer*-[$W(C_2H_4)_2(CO)(PMe_3)_3$] (4).** Carbon monoxide was bubbled at room temperature for 2–3 min through a solution of **3** in petroleum ether (0.5 g, ca. 1 mmol; 20 mL). The solution became almost colorless, and the solvent was removed by pumping under vacuum. The white residue was extracted with petroleum ether (20 mL) and centrifuged, and the supernatant clear solution was concentrated in vacuo and cooled at −20 °C. Colorless crystals of **4** (0.45 g) were obtained from this and a subsequent crystallization of the mother liquor, making a total yield of 90%. IR (Nujol): 3050 w, 3010 w cm^{-1} (ν(=C—H)). IR (hexane): 1855 s cm^{-1} (ν(C≡O)). ^{1}H NMR (C_6D_6): δ 1.0 (t, 2, PMe_3), 0.8 (d, PMe_3), 1.4, 1.9 (br, C_2H_4). $^{31}P\{^1H\}$ NMR (C_6D_6), AX_2 spin system: $\delta(P_A)$ −31.2, $\delta(P_X)$ −35.8, $^2J(P_A-P_X)$ = 18.5 Hz, $^1J(P-W)$ = 186 Hz, $^1J(P_X-W)$ = 234 Hz. $^{13}C\{^1H\}$ NMR: δ 18.5, 22.0, 27.1 (ca. 2:1:1, C_2H_4), 217.8 (d of t, $^2J(C-P_{trans})$ = 37.6 Hz, $^2J(C-P_{cis})$ = 7 Hz, CO). Anal. Calcd for $WC_{14}H_{35}OP_3$: C, 33.9; H, 7.1. Found: C, 33.1; H, 7.0.

***trans,trans,trans*-[$M(C_2H_4)_2(CO)_2(PMe_3)_2$] (M = W (5); M = Mo (6)).** The molybdenum complex (**6**) was prepared by reacting petroleum ether solutions containing ca. 1 mmol of either *trans*-[$Mo(C_2H_4)_2(PMe_3)_4$][7] or *trans,mer*-[$Mo(C_2H_4)_2(CO)(PMe_3)_3$][7] with 2 atm of CO at room temperature for ca. 8 h. The resulting pale yellow solution was evaporated under vacuum to produce a yellow microcrystalline residue, which was recrystallized from petroleum ether at −20 °C. Pale yellow crystals of **6** (0.4 g, 90% yield) were collected and dried in vacuo. The analogous tungsten complex (**5**) can be obtained in 80% yield by using a similar procedure, although 3 atm of CO and longer reaction times (ca. 72 h) are required. Anal. Calcd for $WC_{12}H_{26}O_2P_2$: C, 32.1; H, 5.8. Found: C, 32.6; H, 6.2. IR (Nujol): 3060 w, 3010 w cm^{-1} (ν(=C—H); 1940 w, 1850 s, 1790 sh cm^{-1} (ν(C≡O)). ^{1}H NMR (C_6D_6): δ 0.9 (pseudotriplet, PMe_3), 1.6 (br, C_2H_4). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −32.9 (s, $^1J(P-W)$ = 235 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 208.1 (t, $^2J(C-P)$ = 6 Hz, CO). Due to fluxionality, the signal due to the olefinic carbons cannot be observed. Anal. Calcd for $MoC_{12}H_{26}O_2P_2$: C, 40.0; H, 7.2. Found: C, 40.0; H, 7.3. IR (Nujol): 3060 w, 3010 w cm^{-1} (ν(=C—H)); 1950 m, 1840 s, 1790 m cm^{-1} (ν(C≡O)). ^{1}H NMR (C_6H_6): δ 1.0 (t, PMe_3), 2.1 (t, $^3J(H-P)$ = 5 Hz, C_2H_4). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −0.3

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Table III. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

compd	$[W(N_2)(PMe_3)_5]$ (**2**)	$[W(C_2H_4)_2(PMe_3)_4]$ (**3**)
mol wt	592.3	544.3
space group	*Pnma*	$P2_1/n$
cell const (23 ± 1 °C)		
a, Å	21.990 (6)	10.130 (3)
b, Å	12.108 (3)	13.699 (4)
c, Å	9.722 (2)	17.029 (6)
β, deg		98.84 (2)
cell vol, Å^3	2588.5	2335.1
molecules/unit cell	4	4
ρ(calcd), g cm^{-3}	1.52	1.53
μ(calcd), cm^{-1}	50.29	54.35
max/min transmissn factors	0.86/0.62	0.79/0.63
radiation	Mo K*α* (0.71073 Å)	Mo K*α* (0.71073 Å)
monochromator	graphite	graphite
max cryst dimens, mm	0.30 × 0.88 × 0.95	0.43 × 0.85 × 0.55
scan width	0.80 + 0.20 tan *θ*	0.90 + 0.20 tan *θ*
scan rate, deg min^{-1}	0.4–20.0 (variable)	0.4–20.0 (variable)
std reflcns	(004), (0,12,0), (18,0,0)	(400), (0,10,0)
decay of stds, %	±2	±2
reflcns measd	2452	1778
2*θ* range, deg	≤50	≤36
reflcns collcd	1753	1465
no. of params var	121	190
GOF	4.43	3.26
R	0.041	0.028
R_w	0.054	0.032

Table IV. Final Fractional Coordinates for $[W(N_2)(PMe_3)_5]$ (**2**)

atom	*x/a*	*y/b*	*z/c*
W	0.38579 (3)	0.2500	0.27705 (6)
P(1)	0.3545 (2)	0.2500	0.0327 (4)
P(2)	0.4924 (2)	0.2500	0.2050 (5)
P(3)	0.2812 (2)	0.2500	0.3594 (5)
P(4)	0.3857 (2)	0.4509 (3)	0.3067 (3)
N(1)	0.4168 (6)	0.2500	0.474 (2)
N(2)	0.4336 (8)	0.2500	0.583 (2)
C(1)	0.276 (1)	0.293 (3)	−0.017 (3)
C(2)	0.380 (1)	0.361 (2)	−0.081 (1)
C(3)	0.550 (1)	0.2500	0.342 (2)
C(4)	0.5268 (9)	0.359 (2)	0.097 (2)
C(5)	0.272 (1)	0.2500	0.552 (2)
C(6)	0.2263 (6)	0.362 (1)	0.322 (1)
C(7)	0.3581 (8)	0.498 (1)	0.480 (1)
C(8)	0.4562 (9)	0.533 (1)	0.313 (2)
C(9)	0.3395 (9)	0.546 (1)	0.198 (2)

Table V. Final Fractional Coordinates for *trans*-$[W(C_2H_4)_2(PMe_3)_4]$ (**3**)

atom	*x/a*	*y/b*	*z/c*
W	−0.03508 (4)	0.14802 (3)	0.21521 (3)
P(1)	0.1938 (3)	0.1285 (2)	0.2884 (2)
P(2)	−0.1337 (3)	0.1134 (3)	0.3367 (2)
P(3)	−0.2538 (3)	0.1200 (3)	0.1281 (2)
P(4)	0.0543 (3)	0.2317 (2)	0.1057 (2)
C(1)	−0.019 (1)	−0.0154 (9)	0.2165 (8)
C(2)	0.010 (1)	0.0169 (9)	0.1417 (8)
C(3)	−0.136 (1)	0.2921 (9)	0.2321 (7)
C(4)	−0.001 (1)	0.2986 (8)	0.2666 (8)
C(5)	0.299 (1)	0.234 (1)	0.3244 (8)
C(6)	0.218 (1)	0.063 (1)	0.3848 (7)
C(7)	0.311 (1)	0.056 (1)	0.2425 (8)
C(8)	−0.315 (1)	0.121 (1)	0.3342 (9)
C(9)	−0.112 (1)	−0.005 (1)	0.3869 (9)
C(10)	−0.085 (1)	0.192 (1)	0.4238 (8)
C(11)	−0.266 (1)	0.126 (1)	0.0208 (7)
C(12)	−0.335 (1)	0.000 (1)	0.1324 (9)
C(13)	−0.395 (1)	0.199 (1)	0.1350 (9)
C(14)	−0.031 (1)	0.341 (1)	0.0607 (7)
C(15)	0.073 (1)	0.166 (1)	0.0139 (8)
C(16)	0.223 (1)	0.286 (1)	0.1228 (8)
H(1)[C(1)]	0.0488	−0.0440	0.2586
H(2)[C(1)]	−0.1043	−0.0615	0.2204
H(3)[C(2)]	0.1201	0.0091	0.1415
H(4)[C(2)]	−0.0522	−0.0042	0.0799
H(5)[C(3)]	−0.1597	0.3371	0.1755
H(6)[C(3)]	−0.1992	0.2879	0.2704
H(7)[C(4)]	0.0619	0.3459	0.2494
H(8)[C(4)]	−0.0148	0.3239	0.3183
H(9)[C(5)]	0.3951	0.2119	0.3442
H(10)[C(5)]	0.2401	0.2766	0.3642
H(11)[C(5)]	0.3182	0.2837	0.2814
H(12)[C(6)]	0.1767	0.0952	0.4265
H(13)[C(6)]	0.2978	0.0655	0.4030
H(14)[C(6)]	0.1677	−0.0010	0.3787
H(15)[C(7)]	0.3252	0.0777	0.1902
H(16)[C(7)]	0.2901	−0.0222	0.2374
H(17)[C(7)]	0.3965	0.0659	0.2835
H(18)[C(8)]	−0.3385	0.1130	0.3781
H(19)[C(8)]	−0.3410	0.1831	0.3211
H(20)[C(8)]	−0.3457	0.0674	0.3046
H(21)[C(9)]	−0.1380	−0.0572	0.3476
H(22)[C(9)]	−0.0203	−0.0080	0.4005
H(23)[C(9)]	−0.1681	−0.0191	0.4152
H(24)[C(10)]	−0.1086	0.1772	0.4720
H(25)[C(10)]	−0.1174	0.2610	0.4162
H(26)[C(10)]	0.0310	0.1984	0.4256
H(27)[C(11)]	−0.3371	0.1014	−0.0146
H(28)[C(11)]	−0.2454	0.1927	−0.0056
H(29)[C(11)]	−0.2046	0.0799	−0.0008
H(30)[C(12)]	−0.4347	0.0015	0.0987
H(31)[C(12)]	−0.3378	−0.0191	0.1901
H(32)[C(12)]	−0.2787	−0.0530	0.1104
H(33)[C(13)]	−0.4133	0.1994	0.1843
H(34)[C(13)]	−0.4727	0.1759	0.1174
H(35)[C(13)]	−0.3679	0.2623	0.1079
H(36)[C(14)]	−0.0154	0.3943	0.1056
H(37)[C(14)]	−0.1266	0.3358	0.0440
H(38)[C(14)]	0.0070	0.3555	0.0090
H(39)[C(15)]	0.1410	0.1305	0.0438
H(40)[C(15)]	−0.0133	0.1241	−0.0054
H(41)[C(15)]	0.1077	0.2028	−0.0156
H(42)[C(16)]	0.2396	0.3372	0.1625
H(43)[C(16)]	0.2434	0.3177	0.0732
H(44)[C(16)]	0.2906	0.2372	0.1400

(s). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 216.5 (t, $^2J(C-P)$ = 10 Hz, CO), 33.1 (br, C_2H_4).

X-ray Data Collection, Structure Determination, and Refinement for $[W(N_2)(PMe_3)_5]$ (2). Single crystals of **2**, straw-colored parallelepipeds, were sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 24 reflections ($\theta > 16°$) accurately centered on the diffractometer are given in Table III. The space group was determined to be the centric *Pnma* and not the acentric $Pn2_1a$ by the successful solution and refinement of this structure and previous refinement of the molybdenum analogue.

One octant of data $(+h,+k,+l)$ was collected on an Enraf-Nonius CAD-4 diffractometer by the θ–2θ scan technique. A summary of data collection parameters is given in Table III. The intensities were corrected for Lorentz and polarization effects. An empirical absorption correction based on ψ scans for two reflections was made.

Calculations were carried out with the SHELX system of computer programs.[26] Neutral-atom scattering factors for W, P, N, C, and H were taken from ref 27, and the scattering was corrected for the real and imaginary components of anomalous dispersion.[27]

$[W(N_2)(PMe_3)_5]$ (**2**) is isostructural with its molybdenum analogue, and the final fractional coordinates for $[Mo(N_2)(PMe_3)_5]$[8] were used as a starting point in the refinement of the tungsten compound. Least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.104$. As in $[Mo(N_2)(PMe_3)_5]$, C(1) was found to be

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(26) G. M. Sheldrick, SHELX system of computer programs for X-ray structure determination, 1976.

(27) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 72, 99, 149.

disordered across the mirror plane and was refined in a general position with an occupancy factor of 0.5. An investigation of the acentric space group $Pn2_1a$ revealed the continued presence of disorder, high correlation values, and a higher R value. Due to the high thermal motion of the carbon atoms, hydrogen atoms could not be located. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.041$ and $R_w = 0.054$. A final difference Fourier showed no feature greater than 0.5 e/Å^3. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was noted. The final values of the positional parameters are given in Table IV.[28]

X-ray Data Collection, Structure Determination, and Refinement for *trans*-[W(C_2H_4)$_2$(PMe_3)$_4$] (3). Single crystals of **3**, red parallelepipeds, were sealed in thin-walled glass capillaries prior to X-ray examination. Final lattice parameters as determined from a least-squares refinement of the angular settings of 15 reflections ($\theta > 18°$) accurately centered on the diffractometer are given in Table III. Systematic absences defined the space group as $P2_1/n$.

Data were collected as described for the previous compound. The intensities were corrected for Lorentz and polarization effects and for absorption. Neutral-atom scattering factors were obtained as noted above. The scattering was corrected for the real and imaginary components of anomalous dispersion.[27]

The positional parameters of the isostructural Mo analogue, *trans*-[Mo(C_2H_4)$_2$(PMe_3)$_4$],[7] were used as a starting point in the refinement of this compound. Least-squares refinement with isotropic thermal parameters led to $R = 0.048$. The hydrogen atoms were located with the aid of a difference Fourier map and included in the refinement with fixed contributions. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.028$ and $R_w = 0.032$. A final difference Fourier showed no feature greater than 0.3 e/Å^3. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was noted. The final values of the positional parameters are given in Table V.[28]

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Registry No. **1**, 84879-22-1; **2**, 84879-24-3; **3**, 84879-23-2; **4**, 98720-85-5; **5**, 98720-86-6; **6**, 98720-87-7; *trans*-[Mo(C_2H_4)$_2$(PMe_3)$_4$], 82044-79-9; *trans,mer*-[Mo(C_2H_4)$_2$(CO)(PMe_3)$_3$], 82044-81-3; $WCl_4(PMe_3)_2$, 86567-86-4; $WCl_3(PMe_3)_3$, 85798-78-3.

Supplementary Material Available: Listings of thermal parameters and observed and calculated structure factors for **2** and **3** (9 pages). Ordering information is given on any current masthead page.

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[28] See paragraph at end of paper regarding supplementary material.

Contribution from the Department of Chemistry and Molecular Structure Center,
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The Tungsten–Tungsten Triple Bond. 11.[1] Ligand Redistribution Reactions Involving Chloride and Dimethylamide Ligands at Dimolybdenum and Ditungsten ($M\equiv M$) Centers Induced by Added Tertiary Phosphines. Preparations and Characterizations of $W_2Cl_2(NMe_2)_4(Me_2PCH_2PMe_2)$, $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2$, and $W_2Cl_4(NMe_2)_2(PMe_2Ph)_2$

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Tertiary phosphines react with $M_2Cl_2(NMe_2)_4$ ($M\equiv M$) compounds (M = Mo and W) in hydrocarbon solvents to give a variety of products depending upon the metal and the phosphine. The bidentate phosphines L-L (L-L = $Me_2PCH_2PMe_2$ and $Me_2PCH_2CH_2PMe_2$) give isolable and kinetically stable 1:1 adducts: $M_2Cl_2(NMe_2)_4$(L-L). The monodentate phosphines L (L = PMe_3 and PMe_2Ph) induce ligand redistribution reactions to give $M_2Cl_3(NMe_2)_3L_2$, $M_2Cl_4(NMe_2)_2L_2$, and $M_2(NMe_2)_6$ compounds. The compounds $M_2Cl_4(NMe_2)_2L_2$, where M = Mo and L = PMe_3 and PMe_2Ph but not where M = W, were found to undergo reductive elimination (by way of β-hydrogen elimination from a NMe_2 ligand) in the presence of added phosphine to give $Mo_2Cl_4L_4$ ($M\overset{4}{-}M$) compounds. The compounds $M_2Cl_2(NMe_2)_4$(L-L) and $M_2Cl_{4-n}(NMe_2)_{2+n}L_2$, where n = 0 or 1, are formulated as compounds containing four-coordinate metal atoms united by M–M triple bonds. This has been verified by single-crystal X-ray diffraction studies for the compounds $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2$ (at –160 °C, a = 11.909 (3) Å, b = 13.271 (4) Å, c = 11.551 (3) Å, α = 104.76 (1)°, β = 108.64 (1)°, γ = 71.09 (1)°, Z = 2, d_{calcd} = 1.916 g cm^{-3}, and the space group is $P\bar{1}$) and $W_2Cl_4(NMe_2)_2(PMe_2Ph)_2$ (at –158 °C, a = 17.624 (8) Å, b = 11.995 (5) Å, c = 14.397 (6) Å, β = 114.29 (3)°, Z = 4, d_{calcd} = 2.093 g cm^{-3}, and the space group is $P2_1/c$). In both molecules the W–W distances, 2.33 (2) Å (averaged), and W–P distances, 2.53 (1) Å (averaged), are similar while the W–N distances are notably shorter when N is bonded to W atoms having two Cl ligands and one PMe_2Ph ligand, 1.93 (1) Å (averaged), relative to W–N distances, 1.99 (1) Å (averaged), involving W atoms bonded to two NMe_2, one Cl, and one PMe_2Ph. In both compounds, the NMe_2 ligands contain trigonal-planar nitrogen atoms and the W–NC_2 units are aligned along with the W–W axis such that the nitrogen lone pairs may interact with the W d_{xy} atomic orbital, the one d orbital not used in either the $M\equiv M$ bond or the four M—L σ bonds. In a formal sense the W–N distance of 1.93 Å corresponds to a W–N double bond and the W–N distance of 1.99 Å to a W–N bond order of $1^1/_2$.

Introduction

Previously it was shown that $M_2Cl_2(NMe_2)_4$ compounds (M = Mo and W) were formed according to the reaction shown in eq 1.[2] The reaction was shown to be catalyzed by the presence of $HNMe_2$. Attempts to prepare $M_2Cl(NMe_2)_5$ failed, yielding only a mixture of $M_2Cl_2(NMe_2)_4$ and $M_2(NMe_2)_6$. Attempts to prepare $M_2Cl_x(NMe_2)_{6-x}$ where $x \geqslant 3$ yielded only pink insoluble polymeric materials. We show here that the dinuclear unit $(M\equiv M)^{6+}$ is preserved in $M_2Cl_x(NMe_2)_{6-x}$ compounds where x = 3 and 4, by the addition of phosphine ligands.

$$M_2(NMe_2)_6 + 2Me_3SiCl \rightarrow M_2Cl_2(NMe_2)_4 + 2Me_3SiNMe_2 \qquad (1)$$

Results and Discussion

Synthesis. $M_2Cl_2(NMe_2)_4$ compounds react with the diphosphines (L-L), $Me_2PCH_2PMe_2$ and $Me_2PCH_2CH_2PMe_2$, to give kinetically inert 1:1 adducts $M_2Cl_2(NMe_2)_4$(L-L). The ^{1}H NMR spectra of these 1:1 adducts leave little doubt that they

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[1] Part 10: Chisholm, M. H.; Heppert, J. A.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1985**, *24*, 3214.

[2] Akiyama, A.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Murillo, C. A. *Inorg. Chem.* **1977**, *16*, 2407.

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