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$W(CO)_3(PMTA)$ ($PMTA = MeN(CH_2CH_2NMe_2)_2$) as a starting material for syntheses of $W(CO)_3(PR_3)_3$, $W(CO)_3(\eta^6\text{-arene})$, and the protonated $W(H)(CO)_3(PR_3)_3^+$ complexes

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Abstract

A new and improved method for the synthesis of $M(CO)_3(PMTA)$ ($M = W$, Mo) from $M(CO)_6$ and PMTA ($MeN(CH_2CH_2NMe_2)_2$) is described. The tridentate nitrogen ligand in $W(CO)_3(PMTA)$ is replaced, under relatively mild conditions, by tertiary phosphines (PMe_3, PEt_3, PMe_2Ph, $PMePh_2$, $PhP(CH_2CH_2PPh_2)_2$, $CH_3C(CH_2PPh_2)_3$, and $Ph_2P(CH_2)_nPPh_2$ where $n = 1$, 2) and arenes (C_6H_6, MeC_6H_5, p-$Me_2C_6H_4$, C_6Me_6, C_6H_5Cl), which provides a general synthetic method for the preparation of $W(CO)_3(PR_3)_3$ and $W(CO)_3(\eta^6\text{-arene})$ complexes. The reactions of $W(CO)_3(L)_3$ [$L = PMe_3$, PEt_3, PMe_2Ph, $PMePh_2$, $PhP(CH_2CH_2PPh_2)_2$, and $CH_3C(CH_2PPh_2)_3$] with CF_3SO_3H in CH_2Cl_2 solution yield the hydrido derivatives $W(H)(CO)_3(L)_3^+$ which were characterized by their ^1H and ^{31}P NMR spectra at different temperatures. These studies show the $W(H)(CO)_3(L)_3^+$ complexes to be fluxional as a result of both hydride and phosphine ligand migration.

Introduction

The direct synthesis of $W(CO)_3L_3$ complexes, where L is a phosphorus donor ligand, from $W(CO)_6$ and L generally requires forcing conditions and leads to a mixture of products [1]. In the cases of the tridentate phosphines $CH_3C(CH_2PPh_2)_3$ and $PhP(CH_2CH_2PPh_2)_2$, the corresponding tricarbonyl derivatives have been synthesized under thermal conditions (~ 150 °C, 50–150 h) in reasonable yield [2,3]. Phosphine substitutions of $W(CO)_6$ have also been catalyzed by $NaBH_4$ to give *fac*-$W(CO)_3L_3$ [4a]. The complexes $W(CO)_3(PMePh_2)_3$ and $W(CO)_3(PMe_2Ph)_3$ have been prepared by this method in about 65% yield; however, the yield was considerably lower (25%) in the case of the more basic phosphine PEt_3 [4a]. The insoluble $[W(CO)_3(pic)]_n$ reacts with phosphines to give $W(CO)_3(PR_3)_3$ in moderate yields [4b]. Alternatively, $W(CO)_3(CH_3CN)_3$ and $W(CO)_3(cht)$ (cht = cycloheptatriene) upon reaction with L give $W(CO)_3L_3$ complexes under relatively

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mild conditions and in good yields [5–7]. However, the syntheses of $W(CO)_3(CH_3CN)_3$ [8] and the related nitrile derivatives $W(CO)_3(RCN)_3$ (R = Et, Pr) [9] from $W(CO)_6$ require long reaction times (4–14 days) in refluxing RCN, and $W(CO)_3$(cht) is prepared from $W(CO)_3(CH_3CN)_3$.

The complexes $W(CO)_3$(diethylenetriamine) and $W(CO)_3$(1,4,7-triazacyclononane) have been directly synthesized from $W(CO)_6$ in good yield [10,11] but they are not useful synthetic precursors of $W(CO)_3L_3$ because of their insolubilities in nearly all organic solvents. The methyl-substituted diethylenetriamine analog $W(CO)_3$(PMTA) (**1a**) (PMTA = pentamethyldiethylenetriamine, $MeN(CH_2CH_2NMe_2)_2$), which was previously synthesized from $W(CO)_3(CH_3CN)_3$ [12], is more soluble in polar solvents and has been used to prepare tricarbonyl-metallates of the general formula $[NR_4]_n[M(CO)_3X]_n$ ($n = 3, 4$; X = OR, SR, OH, H) [12–14].

In this paper we describe a new, improved procedure for the direct synthesis of $W(CO)_3$(PMTA) (**1a**) and $Mo(CO)_3$(PMTA) (**1b**) from $W(CO)_6$ and $Mo(CO)_6$. Also, it is demonstrated that **1a** is a useful precursor to a variety of phosphine and arene tricarbonyl derivatives $W(CO)_3L_3$ and $W(CO)_3(\eta^6\text{-arene})$. Protonation reactions of many of these tricarbonyl derivatives are also presented.

Experimental

General procedures

All reactions and chromatographic separations were carried out under an atmosphere of prepurified N_2 by using standard inert atmosphere and Schlenk [15] techniques. Tetrahydrofuran (THF) and Et_2O were distilled under N_2 from Na/benzophenone. Pentane, hexane, and CH_2Cl_2 were distilled from CaH_2 under N_2; CF_3SO_3H was distilled under argon before use. Unless mentioned otherwise, reagent grade chemicals were used without further purification. Trimethylphosphine was prepared by reaction of methyl Grignard reagent and triphenyl phosphite [16]. PMTA is available from Alfa Products.

Infrared spectra were obtained by using a Bio-Rad FTS-7 FT-IR spectrophotometer. The ^1H NMR data were recorded on a Nicolet NT-300 300 MHz instrument and the $^{31}P\{H\}$ NMR data were obtained on a Varian VXR-300 spectrometer using H_3PO_4 (85%) as an external reference. Deuterated solvents, namely CD_2Cl_2 and $CDCl_3$, were used as internal locks; ^1H chemical shifts are in δ units relative to $SiMe_4$ (TMS). Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

The known complexes $M(CO)_3$(PMTA) (**1a–b**) [12] [M = W (**1a**), Mo (**1b**)], $W(CO)_3(L)_3$ (**2a–d**) [1,4,17] [L = PMe_3 (**2a**), PEt_3 (**2b**), PMe_2Ph (**2c**), $PMePh_2$ (**2d**)], $W(CO)_3[PhP(CH_2CH_2PPh_2)_2]$ (**3a**) [3], $W(CO)_3[CH_3C(CH_2PPh_2)_3]$ (**3b**) [2], $W(CO)_3(\eta^1\text{-dppm})(\eta^2\text{-dppm})$ (**4a**) [6] (dppm = $Ph_2PCH_2PPh_2$), $W(CO)_3(\eta^1\text{-dppe})(\eta^2\text{-dppe})$ (**4b**) [7] (dppe = $Ph_2PCH_2CH_2PPh_2$), $W(CO)_3(\eta^6\text{-arene})$ (**6a–d**) [7,18] [arene = C_6H_6 (**6a**), MeC_6H_5 (**6b**), $p\text{-}Me_2C_6H_4$ (**6c**), C_6Me_6 (**6d**)] were identified by comparison of their spectroscopic data with those reported in the literature.

Synthesis of $W(CO)_3$(PMTA) (1a)

Sublimed $W(CO)_6$ (2.74 g, 7.79 mmol) and PMTA (1.40 g, 8.0 mmol) were heated at reflux in n-decane (60 mL) for 3–4 h, while occasionally returning the sublimed $W(CO)_6$ to the reaction solution by scraping the condenser walls. A yellow precipitate formed during the reaction. The mixture was then cooled in an ice bath, and the yellow solid was filtered and washed with hexanes until the hexane wash was colorless. The product was dissolved in CH_2Cl_2, and the solution was filtered through alumina. Evaporation of the solvent under vacuum gave a yellow microcrystalline solid which was further recrystallized from CH_2Cl_2–hexane at −20 °C. Yield: 2.88 g (84%). ^{1}H NMR (CD_2Cl_2): δ 3.10 (s, 6H, NMe_2), 3.02 (s, 3H, NMe), 2.62 (s, 6H, NMe_2), 2.70–2.91 (m, 8H, CH_2). Anal. Found: C, 32.18; H, 5.23. $C_{12}H_{23}N_3O_3W$ calc.: C, 32.67; H, 5.25%.

*Synthesis of $Mo(CO)_3(PMTA)$ (**1b**)*

This synthesis was carried out as described for the W analogue by starting with $Mo(CO)_6$ (2.12 g, 8.03 mmol) and PMTA (1.40 g, 8.0 mmol) and refluxing for 2–3 h. Yield: 2.30 g (81%). ^{1}H NMR (CD_2Cl_2): δ 2.91 (s, 3H, NMe), 2.90 (s, 6H, NMe_2), 2.64 (s, 6H, NMe_2), 2.66–2.80 (m, 8H, CH_2).

Synthesis of fac-*$W(CO)_3(L)_3$*

fac-*$W(CO)_3(PMe_3)_3$ (**2a**).* To a stirred suspension of $W(CO)_3$(PMTA) (0.46 g, 1.04 mmol) in 30 mL of THF was added PMe_3 (0.27 g, 3.50 mmol), and the mixture was heated at reflux for 30 min. The solvent was removed under vacuum, and the residue was washed with hexanes and then redissolved in CH_2Cl_2. This solution was filtered through alumina and evaporated to dryness under vacuum. Recrystallization of the residue from CH_2Cl_2–hexane at −20 °C afforded white crystals (0.38 g, 73%) of **2a**. ^{1}H NMR (CD_2Cl_2): δ 1.52 (m, CH_3). ^{31}P{H} NMR ($CDCl_3$): δ −44.60 (s, J(PW) = 216 Hz, ^{183}W satellites). The other *fac*-$W(CO)_3(L)_3$ complexes were obtained by analogous procedures.

fac-*$W(CO)_3(PEt_3)_3$ (**2b**).* Yield 87%. ^{1}H NMR (CD_2Cl_2): δ 1.85–1.76 (m, CH_2), 1.09 (dt, J(PH) = 13 Hz, J(HH) = 8 Hz, CH_3). ^{31}P{H} NMR ($CDCl_3$): δ − 11.09 (s, J(PW) = 213 Hz, ^{183}W satellites).

fac-*$W(CO)_3(PMe_2Ph)_3$ (**2c**).* Yield 69%. ^{1}H NMR (CD_2Cl_2): δ 7.34–7.25 (m, Ph), 1.53 (m, Me). Anal. Found: C, 47.84; H, 5.05. $C_{27}H_{33}O_3P_3W$ calc.: C, 47.53; H, 4.88%.

fac-*$W(CO)_3(PMePh_2)_3$ (**2d**).* A longer reaction time (2 h) was required in this case. Yield 77%. ^{1}H NMR (CD_2Cl_2): δ 7.30–7.21 (m, Ph); 1.81 (m, Me).

Synthesis of fac-*$W(CO)_3[PhP(CH_2CH_2PPh_2)_2]$ (**3a**)*

A mixture of $W(CO)_3$(PMTA) (0.70 g, 1.59 mmol) and triphos (0.85 g, 1.60 mmol; triphos = $PhP(CH_2CH_2PPh_2)_2$) was refluxed in THF (40 mL) for 3 h. The solvent was evaporated under vacuum, and the residue was washed with hexanes and then redissolved in CH_2Cl_2. After the solution was filtered through alumina, the solvent was removed under vacuum. The residue was recrystallized from CH_2Cl_2–hexane at −20 °C, yielding **3a** as very pale yellow crystals (0.82 g, 64%). ^{1}H NMR (CD_2Cl_2): δ 7.85–6.96 (m, 25H, Ph), 2.82–2.47 (m, 4H, PCH_2), 2.15–1.96 (m, 4H, PCH_2). ^{31}P{H} NMR (CD_2Cl_2) [3b]: δ 71.24 (t, PPh, J(PP) = 5.9 Hz; J(PW) = 223 Hz, ^{183}W satellites), 39.63 (d, PPh_2, J(PP) = 5.9 Hz; J(PW) = 220 Hz, ^{183}W satellites).

Synthesis of fac-*$W(CO)_3[CH_3C(CH_2PPh_2)_3]$ (**3b**)*

The reaction was carried out as described above for the synthesis of **3a**, starting from $W(CO)_3$(PMTA) (0.58 g, 1.31 mmol) and $CH_3C(CH_2PPh_2)_3$ (0.87 g, 1.40

mmol). A longer reaction time (8 h) was required in this case. White crystals of **3b** were obtained (0.62 g, 53%). ^{1}H NMR (CD_2Cl_2): δ 7.34–7.10 (m, 30H, Ph), 2.37 (d, J(PH) = 25 Hz, 6H, CH_2P), 1.45 (q, J(PH) = 3 Hz, 3H, CH_3).

Synthesis of mer-*W(CO)$_3$(η^1-dppm)(η^2-dppm) (**4a**)*

A mixture of $W(CO)_3$(PMTA) (0.61 g, 1.38 mmol) and dppm (1.07 g, 2.80 mmol; dppm = $Ph_2PCH_2PPh_2$) in THF (35 mL) was heated at reflux temperature for about 4 h. The solvent was then removed under vacuum and the oily residue was chromatographed on a neutral alumina column (2.5 × 9 cm). Elution with CH_2Cl_2–hexanes (1 : 4) gave a yellow fraction which was collected and evaporated to dryness. The residue was recrystallized from CH_2Cl_2–hexanes at $-20\,^\circ$C, affording yellow crystals of **4a** (0.90 g, 63%). ^{31}P{H} NMR ($CDCl_3$): δ 21.3 (ddd, J(PP) = 62, 23, 68 Hz, η^1-dppm, coordinated P), -11.0 (dd, J(PP) = 68, 29 Hz, η^2-dppm, P *trans* to η^1-dppm), -23.6 (dd, J(PP) = 23, 29 Hz, η^2-dppm P *cis* to η^1-dppm), -24.9 (d, J(PP) = 62 Hz, η^1-dppm, uncoordinated P). ^{1}H NMR (CD_2Cl_2): δ 7.61–7.03 (m, Ph), 5.02 (t, J(PH) = 9 Hz, CH_2 of η^2-dppm), 3.20 (m, CH_2 of η^1-dppm).

Synthesis of fac-*W(CO)$_3$(η^1-dppe)(η^2-dppe) (**4b**)*

The compound $W(CO)_3$(PMTA) (**1a**) (0.45 g, 1.02 mmol) and dppe (0.81 g, 2.04 mmol; dppe = $Ph_2PCH_2CH_2PPh_2$) were refluxed in THF (30 mL) for 4 h. After cooling, the solvent was removed under vacuum and the residue was chromatographed on an alumina column (2.5 × 9 cm). Elution with CH_2Cl_2–hexanes (1 : 1) gave a yellow band which was collected and evaporated to dryness. Recrystallization of the residue from CH_2Cl_2–hexanes at $-20\,^\circ$ afforded yellow crystals of **4b** (0.74 g, 68%). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 35.6 (d, J(PP) = 21 Hz, η^2-dppe), 9.5 (dt, J(PP) = 21, 30 Hz, η^1-dppe, coordinated P), -11.9 (d, J(PP) = 30 Hz, η^1-dppe, uncoordinated P). ^{1}H NMR (CD_2Cl_2): δ 7.65–6.62 (m, 20H, Ph), 2.51 (m, 4H, CH_2 of η^2-dppe), 2.12, 1.64 (m, 4H, CH_2 of η^1-dppe).

Synthesis of mer-*W$_2$(CO)$_6$(depe)$_3$ (**5**)*

To a stirred suspension of $W(CO)_3$(PMTA) (**1a**) (0.51 g, 1.15 mmol) in toluene (30 mL), depe (0.47 g, 2.30 mmol; depe = $Et_2PCH_2CH_2PEt_2$) was added and the mixture was heated at reflux temperature for 1 h. The solution was filtered through alumina, and the solvent was removed under vacuum. Recrystallization of the residue from CH_2Cl_2–hexanes yielded yellow crystals of **5** (0.47 g, 71%). ^{31}P{H} NMR ($CDCl_3$): δ 38.6 (d br, J(PP) = 58 Hz, η^2-depe, P *trans* to the μ-depe; J(PW) = 262 Hz, ^{183}W satellites); 24.2 (d br, J(PP) = 14 Hz, η^2-depe, P *cis* to μ-depe; J(PW) = 215 Hz, ^{183}W satellites); 3.4 (dm, J(PP) = 58 Hz, μ-depe; J(PW) = 285 Hz, ^{183}W satellites). Anal. Found: C, 37.78; H, 6.45. $C_{36}H_{72}W_2O_6P_6$ calc.: C, 37.45; H, 6.29%.

Synthesis of W(CO)$_3$(η^6-arene)

*W(CO)$_3$(η^6-C_6H_6) (**6a**).* To a stirred suspension of $W(CO)_3$(PMTA) (**1a**) (0.45 g, 1.02 mmol) in benzene (20 mL), $BF_3 \cdot OEt_2$ (0.43 g, 3.0 mmol) was added, and the mixture was heated at reflux for 2 h. The yellow solution was cooled to room temperature, filtered and evaporated to dryness under vacuum. The residue was chromatographed on an alumina column (2.5 × 8 cm), eluting with a CH_2Cl_2–

hexanes mixture (1 : 4). The first yellow fraction was collected and evaporated under vacuum. Recrystallization of the residue from CH_2Cl_2–pentane at −20 °C gave 95 mg (27%) of yellow crystals of **6a**. ^1H NMR ($CDCl_3$): δ 5.38 (s, C_6H_6).

A second yellow fraction was eluted with CH_2Cl_2 and evaporated under vacuum. Crystallization of the residue from CH_2Cl_2–hexanes at −20 °C gave yellow crystals of $W(CO)_4(PMTA)$ (0.09 g, 21%). IR (CH_2Cl_2): $\nu(CO)$ 2009 (w), 1876 (vs), 1824 (ms) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.06, 3.03 (s, NMe_2); 2.77, 2.75 (s, NMe_2); 2.93 (s, NMe); 3.01–2.83 (m, CH_2). Anal. Found: C, 33.19; H, 4.93. $C_{13}H_{23}N_3O_4W$ calc.: C, 33.27; H, 4.94%.

The other $W(CO)_3(\eta^6\text{-arene})$ complexes were obtained by analogous procedures.

*$W(CO)_3(\eta^6\text{-}MeC_6H_5)$ (**6b**).* Yield 56%. ^1H NMR ($CDCl_3$): δ 5.54–5.21 (m, 5H, C_6H_5), 2.41 (s, 3H, CH_3).

*$W(CO)_3(\eta^6\text{-p-}Me_2C_6H_4)$ (**6c**).* To a stirred suspension of $W(CO)_3(PMTA)$ (0.62 g, 1.40 mmol) in THF (30 mL) were added *p*-xylene (1.0 mL, 8.16 mmol) and $BF_3 \cdot OEt_2$ (0.60 g, 4.2 mmol), and the mixture was refluxed for 2 h. Purification of the reaction product as described above yielded yellow crystals of **6c** (0.34 g, 18%). ^1H NMR ($CDCl_3$): δ 5.42 (s, 4H, C_6H_4), 2.32 (s, 6H, CH_3).

*$W(CO)_3(\eta^6\text{-}C_6Me_6)$ (**6d**).* A procedure similar to that described above for the synthesis of **6c** was followed. Yield 16%. ^1H NMR ($CDCl_3$): δ 2.43 (s, Me).

*$W(CO)_3(\eta^6\text{-}C_6H_5Cl)$ (**6e**).* The compound $W(CO)_3(PMTA)$ (**1a**) (0.49 g, 1.11 mmol) and $BF_3 \cdot OEt_2$ (0.47 g, 3.3 mmol) were heated in chlorobenzene (20 mL) at 70 °C for 3 h. Purification of the reaction product as described above yielded $W(CO)_3(\eta^6\text{-}C_6H_5Cl)$ as yellow crystals (26 mg, 7%). ^1H NMR ($CDCl_3$): δ 5.51 (m, C_6H_5Cl). Anal. Found: C, 28.63; H, 1.34. $C_9H_5ClO_3W$ calc.: C, 28.41; H, 1.32%.

Results and discussion

Syntheses of W(CO)$_3$(PMTA) (1a) and Mo(CO)$_3$(PMTA) (1b)

The reaction of $W(CO)_6$ with PMTA in refluxing n-decane for 3–4 h results (eq. 1) in a high yield (84%) of the easily purified $W(CO)_3(PMTA)$.

$$W(CO)_6 + PMTA \xrightarrow{\text{n-decane, } \Delta} \underset{\textbf{(1a)}}{fac\text{-}W(CO)_3(PMTA)} + 3\ CO \qquad (1)$$

$$PMTA = MeN(CH_2CH_2NMe_2)_2$$

The analogous reaction of $Mo(CO)_6$ affords $Mo(CO)_3(PMTA)$ (**1b**) in 81% yield. Under the same reaction conditions $Cr(CO)_6$ largely decomposed, yielding a black insoluble solid together with a mixture of $Cr(CO)_4(PMTA)$ and $Cr(CO)_3(PMTA)$, whose identities are supported by their IR and ^1H NMR spectra which are similar to those of the W analogs.

Although complex **1a** was previously prepared in 75–80% yield [12] from the reaction of $W(CO)_3(CH_3CN)_3$ with PMTA, the present method (eq. 1) has the advantages of being a one-step direct procedure from $W(CO)_6$ requiring shorter reaction times (hours instead of days) and giving higher yields.

Synthesis of tungsten carbonyl phosphine complexes

The PMTA ligand in $W(CO)_3(PMTA)$ (**1a**) is easily replaced (eq. 2) by monodentate tertiary phosphines in refluxing THF to afford the corresponding *fac*-

$W(CO)_3(PR_3)_3$ derivatives (**2a–d**) in good yields (70–80%). There was no reaction of **1a** with PPh_3 under the same conditions during 5 h of reflux [19].

$$\underset{(\mathbf{1a})}{fac\text{-}W(CO)_3(PMTA)} + 3PR_3 \xrightarrow[2\text{-}4\ h]{THF,\ \Delta} \underset{(\mathbf{2a\text{-}d})}{fac\text{-}W(CO)_3(PR_3)_3} + PMTA \qquad (2)$$

$PR_3 = PMe_3$ (**2a**), PEt_3 (**2b**), PMe_2Ph (**2c**), $PMePh_2$ (**2d**)

The *fac* geometry of these complexes can be assigned on the basis of their IR spectra (Table 1). The two strong carbonyl absorbances are typical of *fac*-$M(CO)_3L_3$ compounds [20]. The tridentate phosphines $PhP(CH_2CH_2PPh_2)_2$ and $CH_3C(CH_2PPh_2)_3$ react analogously with **1a** affording *fac*-$W(CO)_3[PhP(CH_2CH_2PPh_2)_2]$ (**3a**) and *fac*-$W(CO)_3[CH_3C(CH_2PPh_2)_3]$ in 64% and 53% yield, respectively.

The complexes *fac*-$W(CO)_3(\eta^1\text{-dppm})(\eta^2\text{-dppm})$ (**4a**) and *fac*-$W(CO)_3(\eta^1\text{-dppe})(\eta^2\text{-dppe})$ (**4b**) were recently synthesized in good yields (65–77%) from $W(CO)_3(cht)$ and dppm or dppe in CH_2Cl_2 or MeOH solution [6]. The *fac*-isomer (**4a**) was converted, upon heating at reflux in benzene, to the *mer*-isomer [6a]. We have found that complexes *mer*-**4a** and *fac*-**4b** can be prepared analogously in good yields (60–70%) by reacting $W(CO)_3(PMTA)$ (**1a**) with the corresponding bidentate phosphine in refluxing THF. The reaction between **1a** and $Et_2PCH_2CH_2PEt_2$ (depe) in toluene at reflux temperature for about 1 h resulted in the formation of *mer*-$W_2(CO)_6(depe)_3$ (**5**) in 71% yield.

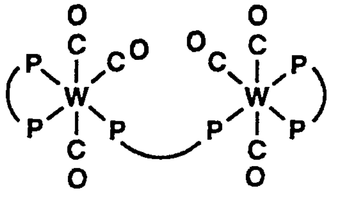

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Table 1

Infrared data for the complexes in CH_2Cl_2

Complex	ν(CO), cm^{-1}
$W(CO)_3(PMTA)$ (**1a**)	1898 (s), 1764 (s, br), 1744 (sh)
$Mo(CO)_3(PMTA)$ (**1b**)	1907 (s), 1774 (s, br), 1755 (sh)
fac-$W(CO)_3(PMe_3)_3$ (**2a**)	1922 (s), 1818 (s, br)
fac-$W(CO)_3(PEt_3)_3$ (**2b**)	1916 (s), 1808 (s, br)
fac-$W(CO)_3(PMe_2Ph)_3$ (**2c**)	1926 (s), 1823 (s, br)
fac-$W(CO)_3(PMePh_2)_3$ (**2d**)	1931 (s), 1832 (s, br)
fac-$W(CO)_3[PhP(CH_2CH_2PPh_2)_2]$ (**3a**)	1932 (s), 1834 (s, br)
fac-$W(CO)_3[CH_3C(CH_2PPh_2)_3]$ (**3b**)	1930 (s), 1835 (s, br)
mer-$W(CO)_3(\eta^1\text{-dppm})(\eta^2\text{-dppm})$ (**4a**)	1958 (w), 1856 (s), 1833 (sh)
fac-$W(CO)_3(\eta^1\text{-dppe})(\eta^2\text{-dppe})$ (**4b**)	1931 (s), 1835 (s, br)
mer-$W_2(CO)_6(depe)_3$ (**5**)	1940 (w), 1829 (s, br)
$W(CO)_3(\eta^6\text{-}C_6H_6)$ (**6a**)	1968 (s), 1886 (s, br)
$W(CO)_3(\eta^6\text{-}MeC_6H_5)$ (**6b**)	1965 (s), 1880 (s, br)
$W(CO)_3(\eta^6\text{-p-}Me_2C_6H_4)$ (**6c**)	1960 (s), 1875 (s, br)
$W(CO)_3(\eta^6\text{-}C_6Me_6)$ (**6d**)	1942 (s), 1854 (s, br)
$W(CO)_3(C_6H_5Cl)$ (**6e**)	1977 (s), 1899 (s, br)

Analogous reactions between $W(CO)_3(cht)$ and dmpm (dmpm = $Me_2PCH_2PMe_2$) or $W(CO)_3(NCMe)_3$ and dmpe (dmpe = $Me_2PCH_2CH_2PMe_2$) are known [21] to yield the dimers *fac*-$W_2(CO)_6(dmpm)_3$ and *fac*-$W_2(CO)_6(dmpe)_3$, respectively. In our case the *mer* geometry has been assigned to **5** because of the similar ν(CO) absorptions of **5** and *mer*-**4a** (1940w, 1829s, br versus 1958 w, 1856 s, 1833sh cm^{-1}). Furthermore, the ^{31}P NMR spectrum of **5** (see Experimental section) shows three sets of signals corresponding to the three inequivalent P atoms of the *mer* isomer, while only two would be expected for the *fac* isomer [21]. When the reaction of **1a** and depe was performed in refluxing THF, the intermediate *fac* isomer of **5** could be detected by IR spectroscopy [ν(CO) (CH_2Cl_2): 1918s, 1819s(br) cm^{-1}].

Based on the above studies, $W(CO)_3(PMTA)$ has the following advantages over $W(CO)_3(CH_3CN)_3$ and $W(CO)_3(cht)$ for the synthesis of $W(CO)_3(PR_3)_3$ complexes: (1) The synthesis of $W(CO)_3(PMTA)$ requires much less reaction time than either of the other compounds. (2) It is easily separated by filtration from the reaction mixture. (3) It may be stored indefinitely under a nitrogen atmosphere and is moderately air-stable. In its reactions with phosphine, it gives yields of $W(CO)_3(PR_3)_3$, which are high and comparable to those obtained from $W(CO)_3(CH_3CN)_3$ and $W(CO)_3(cht)$.

Reactions of $W(CO)_3(PMTA)$ (1a) with arenes

High temperatures and long reaction times are generally required to synthesize $W(CO)_3(\eta^6\text{-arene})$ from $W(CO)_6$, and for arene = $\eta\text{-}C_6Me_nH_{6-n}$ ($n = 0\text{–}6$), yields are generally lower than 10% [18,19]. Using $W(CO)_3(CH_3CN)_3$ as the starting material [18], milder conditions ($\leqslant 130\,^\circ C$) gave higher yields of the products; reactions of arenes with $W(CO)_3(py)_3$ were very slow and gave poor yields [22]. We have investigated the reactivity of **1a** towards arenes and found that the PMTA ligand is replaced by arenes in a $BF_3 \cdot Et_2O$-promoted reaction (eq. 3).

$$\underset{\textbf{(1a)}}{W(CO)_3(PMTA)} \xrightarrow[\text{THF, }\Delta,\ -\text{PMTA}]{\text{arene, }BF_3\cdot OEt_2} \underset{\textbf{(6a–e)}}{W(CO)_3(\eta^6\text{-arene})} \qquad (3)$$

arene = C_6H_6 (**6a**), MeC_6H_5 (**6b**), *p*-$Me_2C_6H_4$ (**6c**), C_6Me_6 (**6d**), C_6H_5Cl (**6e**)

The π-arene derivatives are obtained in yields (20–60%) comparable to those obtained in their syntheses from $W(CO)_3(CH_3CN)_3$ [7]. In all cases, the preparations of $W(CO)_3(\eta^6\text{-arene})$ described by eq. 3 are accompanied by the formation of variable amounts (10–30%) of $W(CO)_4(PMTA)$. By refluxing in n-decane, $W(CO)_4(PMTA)$ could be almost quantitatively converted to **1a**.

Very few examples of π-arene tungsten complexes containing arenes with electron-withdrawing groups are known [18]. Unfortunately, the method described by eq. 3 also provides $W(CO)_3(C_6H_5Cl)$ (**6e**) [23] only in low yield (7%). The reaction between **1a** and $C_6H_5NO_2$ under the same conditions failed, however, to give the expected arene tricarbonyl derivative.

Protonation of the complexes

Approximately 0.01 *M* solutions of the above-described tricarbonyl complexes (**1a**, **2**, **3** and **5**) in CH_2Cl_2 were treated with one equivalent of CF_3SO_3H at room temperature. The metal center was quantitatively protonated and the following cationic hydride products were detected spectroscopically (Table 2): $W(H)(CO)_3(PMTA)^+$ (**7**); $W(H)(CO)_3(L)_3^+$ (**8a–d**) [L = PMe_3 (**8a**), PEt_3 (**8b**), PMe_2Ph (**8c**), $PMePh_2$ (**8d**)], $W(H)(CO)_3[PhP(CH_2CH_2PPh_2)_2]^+$ (**9a**), $W(H)(CO)_3[CH_3C(CH_2PPh_2)_3]^+$ (**9b**), and $W_2(H)(CO)_6(depe)_3^+$ (**10**). These protonated complexes were insufficiently stable to be isolated. The $\nu(CO)$ patterns of the cationic complexes (**8–9**) differ greatly from those of the parent compounds, indicating that substantial changes in the geometries of the complexes occur upon protonation. Similarities in wavenumbers and relative intensities in the $\nu(CO)$ spectra of the cationic **8**, **9a**, and **10** (Table 2) and complexes of the type *mer*-$[M(CO)_3P_3]^+$ (M = Cr, Mo; P = phosphines and phosphites) [24] (e.g., *mer*-$[Cr(CO)_3(P(OMe)_2Ph)_3]^+$ has $\nu(CO)$ at 2042m, 1970m, 1911s cm^{-1} in CH_2Cl_2 solution) suggest that the CO groups in the cationic hydride complexes occupy nearly co-planar positions. The $\nu(CO)$ pattern of $W(H)(CO)_3[CH_3C(CH_2PPh_2)_3]^+$ (**9b**), however, is very similar to that of its unprotonated precursor **3b**, indicating that it retains the geometry in which the three CO groups are mutually *cis*, as required by the $CH_3C(CH_2PPh_2)_3$ ligand structure.

As for **8** and **9a**, isomerization from *fac* to co-planar CO groups has been observed to occur upon protonation of *fac*-$W(CO)_3(dppm)(PEt_3)$ [25]. The related species *cis*-$M(CO)_2(\widehat{P\ P})_2$ (M = Cr, Mo, W; $\widehat{P\ P}$ = chelating phosphines) are also converted to the *trans*-isomers upon protonation at the metal center [26]. The *fac*-$M(CO)_3(L)_3$ complexes (M = Cr, Mo; L = phosphines) are also known to undergo rapid isomerization to *mer*-$M(CO)_3(L)_3^+$ upon electrochemical oxidation [24].

The hydride resonances observed in the ^1H NMR spectra (Table 2) of the complexes **7–10** indicate that protonation occurs quantitatively at the metal center. The hydride signal for $W(H)(CO)_3[CH_3C(CH_2PPh_2)_3]^+$ (**9b**) consists of a quartet at −4.62 ppm in CD_2Cl_2 due to equal coupling ($J(PH) = 21$ Hz) to the three P atoms. The equivalence of the three phosphorus atoms suggests that the hydride is either located on the C_{3v} axis of the *fac*-$W(CO)_3[CH_3C(CH_2PPh_2)_3]$ unit or the complex is fluxional on the NMR time scale at room temperature. Neither possibility can be excluded because the hydrides of the related complexes **8a**, **8b**, and **9a** are highly fluxional, as described in the studies given below.

The low temperature ^{31}P NMR spectrum (Fig. 1a) of **9a** shows clearly a trio of resolved doublets of doublets arising from three nonequivalent phosphorus nuclei P_A, P_B, and P_C with two-bond scalar couplings $^2J(P_AP_B) = 23$ Hz, $^2J(P_BP_C) = 17$ Hz, and $^2J(P_AP_C) = 37$ Hz. Additional small peaks are assigned as ^{183}W (14.4% abundance) satellites ($J(PW) = 220$ Hz) which confirm a direct one-bond interaction between phosphorus and tungsten. At higher temperature, signals of P_A and P_C become broader (−10 °C) or even almost unobservable (25 °C), while P_B resembles a typical triplet (Fig. 1c). Over a similar temperature range, the hydride resonance in ^1H NMR spectra of **9a** changes from a doublet of doublets into a triplet as the temperature is increased from −35 °C to 37 °C (Fig. 1d–f).

To account for these spectral changes, consider the pentagonal bipyramidal structure of **9a** represented in Fig. 2. While this structure cannot be assigned unequivocally, the P–W–P and P–W–H angles in it are consistent with the observed $^2J(PP)$ and $^2J(HP)$ coupling constants. It is known that $^2J(PP)$ is about 60 Hz for *trans* phosphines (180 °) in tungsten complexes, as observed in **4a** and **5**. On the other hand, $^2J(PP)$ is only about 20 Hz for *cis* phosphines, as in **4a** and **4b**. The $^2J(P_AP_C) = 37$ Hz value in **9a** suggests that the P_A–W–P_C angle is intermediate

Tabel 2

IR and ^{1}H NMR data for the cationic hydride complexes

Complex	IR ν(CO), cm^{-1} [a]	^{1}H NMR, δ ppm [b]	
		Hydride	Other resonances
W(H)(CO)$_3$(PMTA)$^+$ (**7**)	2016(s), 1927(vs), 1893(s)	−3.40 [s]	3.34 [s, NMe], 3.28 [s, NMe$_2$], 2.82 [s, NMe$_2$], 2.86–3.25 [m, CH$_2$]
W(H)(CO)$_3$(PMe$_3$)$_3^+$ (**8a**)	2033(m), 1947(m), 1919(vs)	−3.97 [q, *J*(PH) = 47 Hz]	1.86 [d, *J*(PH) = 9 Hz, CH$_3$]
W(H)(CO)$_3$(PEt$_3$)$_3^+$ (**8b**)	2022(m), 1943(m), 1908(vs)	−3.48, −3.70(br) −3.91	2.06 [m, CH$_2$], 1.17 [m, CH$_3$]
W(H)(CO)$_3$(PMe$_2$Ph)$_3^+$ (**8c**)	2034(m), 1947(m), 1914(vs)	−3.21 [q, *J*(PH) = 47 Hz]	7.47–7.32 [m, Ph] 1.92 [d, *J*(PH) = 9 Hz]
W(H)(CO)$_3$(PMePh$_2$)$_3^+$ (**8d**)	2034(m), 1958(m), 1910(vs)	−1.76, −1.92(br) −2.06(br), −2.23	7.47–7.25 [m, Ph] 2.19 [s, br, CH$_3$]
W(H)(CO)$_3$[PhP(CH$_2$CH$_2$PPh$_2$)$_2$]$^+$ (**9a**)	2038(m), 1976(m), 1918(vs)	−3.67, −3.78(br) −3.89	7.66–7.41 [m, Ph] 3.7 [m, CH$_2$], 2.6 [m, CH$_2$]
W(H)(CO)$_3$[CH$_3$C(CH$_2$PPh$_2$)$_3$]$^+$ (**9b**)	2025(s), 1954(s), 1941(sh)	−4.62 [q, *J*(PH) = 21 Hz]	7.41–7.21 [m, Ph] 2.69 [m, CH$_2$] 1.75 [q, *J*(PH) = 3 Hz, CH$_3$]
W$_2$(H)(CO)$_6$(depe)$_3^+$ (**10**)	2031(m), 1964(m), 1907(vs)	−4.05 [t br, *J*(PH) = 60 Hz]	1.16–1.24 [m, CH$_3$] 1.96–2.23 [m, CH$_2$]
W(H)(CO)$_3$(η^6-C$_6$Me$_6$)$^+$ (**11**)	2057(s), 1982(s, br)	−6.55 [s]	2.58 [s,CH$_3$]

[a] CH$_2$Cl$_2$ solvent. [b] CD$_2$Cl$_2$ solvent.

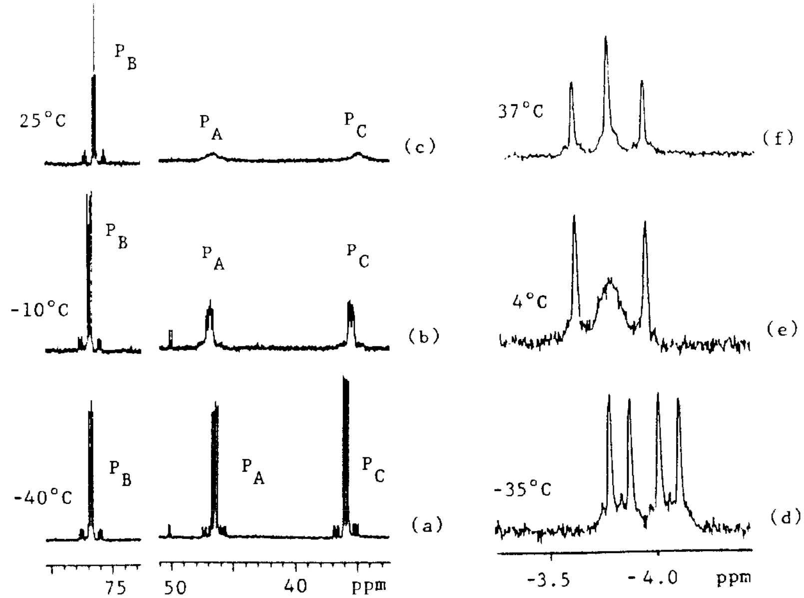

Fig. 1. ^{31}P and ^{1}H NMR spectra of $W(H)(CO)_3[PhP(CH_2CH_2PPh_2)_2]^+$ (**9a**) in CD_2Cl_2 at various temperatures.

between 90° and 180°, as shown in Fig. 2. The other two angles (P_A–W–P_B and P_B–W–P_C) remain close to 90° since $^2J(P_AP_B) = 23$ Hz and $^2J(P_BP_C) = 17$ Hz.

This structure is also supported by ^2J(HP) coupling constants observed in the ^1H NMR spectrum of **9a**. In the α-isomer (Fig. 2) of **9a**, $^2J(H_\alpha P_A) = 46$ Hz and $^2J(H_\alpha P_C) = 18$ Hz, while $^2J(H_\alpha P_B)$ is unresolvably small ($\leqslant 2$ Hz). In the β-isomer, $^2J(H_\beta P_C) = 46$ Hz, $^2J(H_\beta P_A) = 18$ Hz, and $^2J(H_\beta P_B) \leqslant 2$ Hz thus giving the identical pattern as for the α-isomer. The unobservably small $^2J(H_\alpha P_B)$ and $^2J(H_\beta P_B)$ coupling constants are not surprising since the H–W–P_B angle is 90° (Fig. 2), which should give a small coupling constant. An example of this is seen in $[(NP_3)Rh(H)(Cl)]^+$ ($NP_3 = N(CH_2CH_2PPh_2)_3$) [27] where ^2J(HP) is 192.2 Hz when the H and P are *trans* to each other but only 6.8 Hz when they are *cis*.

At low temperatures interconversion of the α and β isomers is slow and the hydride remains in one site sufficiently long (i.e., more than about 1 s), so that the ^1H spectrum shows four peaks arising from coupling with P_A and P_C in states

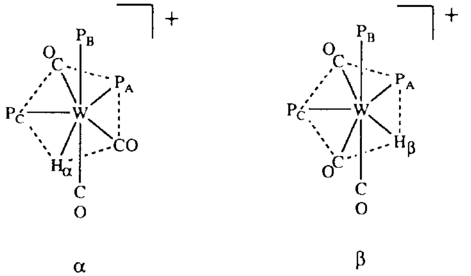

Fig. 2. Proposed pentagonal bipyramidal structures of the $W(H)(CO)_3P_3^+$ complexes.

$|++\rangle$, $|+-\rangle$, $|-+\rangle$ and $|--\rangle$, respectively. At higher temperatures the rate of interconversion increases and at 4 °C the mean lifetime τ is about 5ms. Faster interconversions do not affect the outer peaks in the multiplet (Fig. 1e), because they arise from P_A and P_C in the same state (i.e., $|++\rangle$ and $|--\rangle$). The inner peaks, however, collapse into a broad signal as explained by the following description of the spin precession arising from J couplings. Initially the proton H_α is coupled to P_A in the state $|+\rangle$ and to P_C in the state $|-\rangle$; therefore, the precession frequency is equal to $(1/2)[{}^2J(H_\alpha P_A) - {}^2J(H_\alpha P_C)] = (1/2)(46 - 18)$ Hz $= 14$ Hz in the rotating frame. After the interconversion ($H_\alpha \rightarrow H_\beta$), P_A and P_B remain in the same state and precession continues with the frequency $(1/2)[{}^2J(H_\beta P_A) - {}^2J(H_\beta P_C)] = (1/2)(18 - 46)$ Hz $= -14$ Hz. Intermediate exchange rates lead to spin precession in opposite directions and subsequent broadening of the resonance (Fig. 1e). At higher temperatures (37 °C) the hydride migration in **9a** is so fast ($\tau < 1$ ms), that the net precession apparently stops and a sharp peak becomes indistinguishable from the central resonance in a typical triplet (Fig. 1f) with averaged coupling ${}^2J(HP) = (1/2)[{}^2J(H_\alpha P_A) + {}^2J(H_\beta P_A)] = (1/2)[{}^2J(H_\alpha P_C) + {}^2J(H_\beta P_C)] = 32$ Hz.

The same isomer interconversion also explains the ^{31}P NMR spectra. At low temperatures (-40 °C) all three phosphorus sites are nonequivalent and the resonances are sharp, because isomer interconversion is slow on the NMR time scale (Fig. 1a). Faster motion should make P_A and P_C equivalent, but sufficiently high temperatures could not be reached in this study. Nevertheless, interconversion between the α and β isomers has a noticeable effect on the ^{31}P resonance and the P_A and P_C signals become severely broadened at 25 °C (Fig. 1c) thus indicating "intermediate exchange" between the resonances separated by the chemical shift difference of 10.7 ppm or 1300 Hz. On the other hand, the interconversion is fast enough to average ${}^2J(P_AP_B) = 23$ Hz and ${}^2J(P_BP_C) = 17$ Hz, so that the P_B signal becomes a triplet arising from coupling with apparently equivalent P_A and P_C.

A similar isomer interconversion also explains the temperature-dependent NMR spectra of **8b**; however, this process is much faster than in **9a**. A typical lifetime τ for interconversion of the α and β isomers is about 0.6 ms at -40 °C thus broadening resonances P_A and P_C (Fig. 3a). At higher temperature (-20 °C) the signals become unobservably broad (Fig. 3b), but they reappear as a single peak at 1.9 ppm when the exchange becomes so fast ($\tau = 12$ μs) that the chemical shift difference is also averaged (Fig. 3c). At the highest temperature (45 °C, Fig. 3d) the spectrum shows the onset of another broadening which affects both peaks and must be attributed to an additional exchange process within the molecule. This motion should ultimately lead to equivalence of all three phosphorus sites, but sufficiently high temperatures could not be reached in $CDCl_3$ solution.

However, compound **8a** provides an example of a case where all three phosphorus nuclei become equivalent at high temperature. Figure 4a clearly shows that P_A and P_C are becoming equivalent even at -60 °C as a result of $\alpha \rightleftharpoons \beta$ interconversion (estimated $\tau \approx 10$ μs). At higher temperatures an additional fluxional process starts to broaden the ^{31}P resonances (Figs. 4c and 4d). When the exchange is sufficiently fast ($\tau = 60$ μs at 40 °C), the chemical shift difference is averaged and all three ^{31}P nuclei resonate as a single peak (Fig. 4e) which becomes even narrower when further heating increases the exchange rate (Fig. 4f). The process whereby all three phosphorus nuclei become equivalent probably does not involve a rearrangement of **8a** from a structure in which the three CO groups are approximately

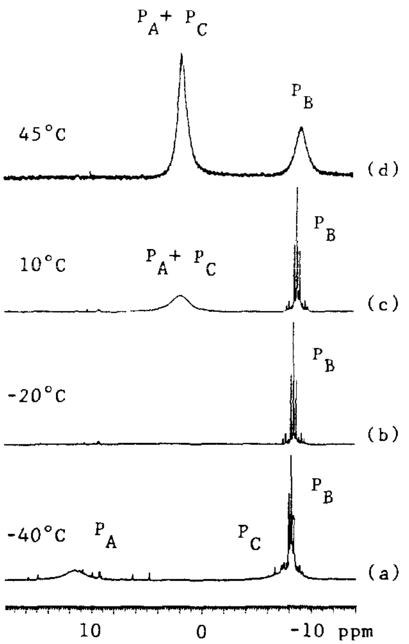

Fig. 3. ^{31}P NMR of $[W(H)(CO)_3(PEt_3)_3]^+$ (**8b**) in $CDCl_3$ at various temperatures.

co-planar (Fig. 2) to one in which they are mutually *cis* since the ν(CO) spectrum of **8a** at room temperature is characteristic (Table 2) of all of the complexes with nearly co-planar CO groups as noted above. Thus, the equivalence of the phosphorus nuclei in the high temperature NMR spectra must be due to a fluxional process involving migration of the phosphorus ligands in the coordination sphere

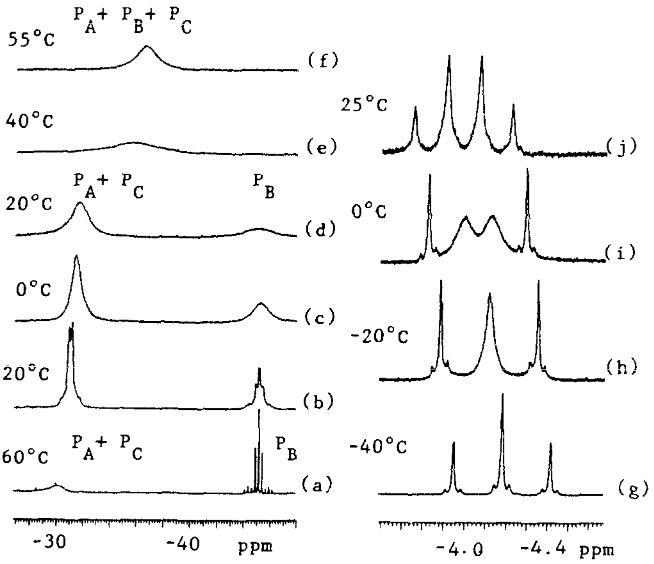

Fig. 4. ^{31}P and ^{1}H NMR spectra of $[W(H)(CO)_3(PMe_3)_3]^+$ (**8a**) in $CDCl_3$ at various temperatures.

without dissociation from the tungsten. Seven-coordinate complexes are known [28] to be fluxional, but it is not possible to specify the detailed mechanism of fluxionality in this case from the available data.

This phosphine fluxionality also explains the appearance of the hydride resonance in ^{1}H NMR spectra of **8a** (Fig. 4). At lower temperatures ($-40\,^\circ$C) only $\alpha \rightleftharpoons \beta$ isomer interconversion is fast; the observed triplet is explained by scalar coupling (^2J(HP) = 70 Hz) with equivalent P_A and P_C, while the interaction with the third phosphorus (P_B) is unresolvable as in the spectrum of **9a** (Fig. 1f). Fluxionality of the PMe_3 ligands causes all three phosphorus nuclei to become equivalent at high temperatures (Fig. 4j), and the coupling pattern resembles a quartet with averaged ^2J(HP) = 47 Hz. Spectra in Figs. 4h and 4i are characteristic of "intermediate" exchange which selectively broadens the inner resonances. The outer peaks represent signals arising from the interaction with all three ^{31}P nuclei in the same state (i.e. $|+++\rangle$ or $|---\rangle$, respectively) and fluxionality within the molecule does not change the precession frequency of the observed ^{1}H nucleus. The position and width of these resonances, therefore, should not be affected by temperature increases which bring the spin system through "slow", "intermediate" and "fast" exchange. This conclusion is unambiguously supported by experimental results in Fig. 4.

These temperature dependent NMR studies of **9a**, **8b**, and **8a** show that two fluxional processes occur; both are intramolecular as indicated by ^{183}W satellites in both the ^{1}H and ^{31}P spectra. Isomer interconversion ($\alpha \rightleftharpoons \beta$) begins at low temperature and the rate increases with the complex in the order: **9a** < **8b** < **8a**. At higher temperatures, phosphorus ligand migration occurs, which makes all three phosphorus donors equivalent; this fluxional process is faster for **8a** than for **8b**. Both the hydride migration and phosphine ligand migration processes are faster for $W(H)(CO)_3(PMe_3)_3^+$ (**8a**) than for $W(H)(CO)_3(PEt_3)_3^+$ (**8b**), perhaps reflecting the bulkier nature of PEt_3 as compared with PMe_3.

In complexes **4a–b**, both the W and the uncoordinated P atom are possible sites of protonation. Treatment of **4a** with an equimolar amount of CF_3SO_3H results in an IR spectrum in the ν(CO) region (1927 m, 1862 s, 1822 m cm^{-1} in CH_2Cl_2) which is similar to that (1958 w, 1856 s, 1833 sh cm^{-1}) of unprotonated **4a** but with ν(CO) absorptions at somewhat higher wavenumber. The ^{1}H NMR spectrum of **4a** with equimolar CF_3SO_3H in CD_2Cl_2 shows no evidence for an upfield hydride signal, but there is a large chemical shift for the methylene protons of the η^1-bonded dppm ligand (4.42 vs 3.20 ppm for **4a**) while the CH_2 resonance of the η^2-dppm ligand changes much less (4.96 vs 5.02 for **4a**). The ^{31}P{H} NMR spectrum of **4a** shows a large shift of the uncoordinated P atom upon protonation (10.63 vs -24.9 ppm for **4a**) while the coordinated P atoms experience much smaller shifts (25.70, -13.92, -26.87 vs. 21.3, -11.0, -23.6 ppm). All of these data indicate that the addition of one equivalent of CF_3SO_3H to **4a** results in protonation of the dangling, uncoordinated phosphorus atom. With a 3 : 1 ratio of CF_3SO_3H to **4a** in CH_2Cl_2, the IR spectrum (2048 m, 1987 m, 1929 s cm^{-1}) in the ν(CO) region exhibits a pattern which is typical of $W(H)(CO)_3(L)_3^+$ complexes such as **8** and **9a** (Table 2) with the structure proposed in Fig. 2. The ^{1}H NMR spectrum of **4a** with three equivalents of CF_3SO_3H shows a very broad resonance at -2.3 ppm. Thus, in excess CF_3SO_3H the tungsten is protonated. Although the metal is less basic than the uncoordinated phosphorus in **4a**, the metal is still sufficiently basic to be protonated even after the phosphorus is protonated.

Treatment of **4b** with one equivalent of CF_3SO_3H also gives protonation of the dangling P atom, but the acid also catalyzes the isomerization of the facial **4b** to the meridional isomer; such an acid-catalyzed isomerization was previously reported for $W(CO)_3(\eta^2\text{-dppm})(PEt_3)$ [25a] and $Mo(CO)_3(dppe)(SO_2)$ [25b]. This isomerization for **4b** is noted in the IR and ^1H NMR spectra, and there is no evidence for upfield hydride signals in the ^1H NMR. Three equivalents of CF_3SO_3H move the $\nu(CO)$ absorptions up to 2045 m, 1983 m, 1919 vs cm^{-1} in CH_2Cl_2, and hydride resonances are observed at -2.51, -2.53 br, -2.73 ppm. Thus, as for **4a**, **4b** is first protonated at the dangling phosphorus and then at the tungsten.

It is known that $M(CO)_2(PPhMe_2)(\eta^6\text{-arene})$ complexes (M = Cr, Mo, W; arene = C_6H_6, mesitylene) are quantitatively protonated at the metal by a four to tenfold molar excess of CF_3SO_3H [29]. Further evidence for the basicity of tricarbonyl(η^6-arene)tungsten(0) complexes comes from their ability to form adducts with Lewis acids such as $AlCl_3$ [30] and their protonation with CF_3SO_3H [31]. We found that the complex $W(CO)_3(\eta^6\text{-}C_6Me_6)$ (**6d**), which is the most basic of the η^6-arene complexes described above, was completely protonated at the metal by treatment with four equivalents of CF_3SO_3H in CH_2Cl_2.

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