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Seven-Coordinate Hydride Complexes of Molybdenum and Tungsten. Crystal and Molecular Structures of $WH(Cl)(CO)_2(PMe_3)_3$

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*Summary: Addition of the hydride reagent $LiBEt_3H$ to solutions of the chlorocarbonyls $MCl_2(CO)_2(PMe_3)_3$ (M = Mo, W) furnishes the seven-coordinate hydrides $MH(Cl)(CO)_2(PMe_3)_3$ (M = Mo (**2a**), W (**2b**)). Further substitution of chloride by hydride does not occur, but upon treatment of **2** with appropriate salts of the anionic bidentate groups (X–X) S_2CNMe_2, S_2CO-i-Pr, S_2COMe, and acac, the corresponding derivatives $MH(X–X)(CO)_2(PMe_3)_2$ (**3–6**) are formed. The tungsten complex **2b** has been characterized by X-ray crystallography. Crystals of **2b** are monoclinic, of space group $P2_1/c$ with unit cell parameters of $a = 14.514(1)$ Å, $b = 8.471(7)$ Å, $c = 16.458(3)$ Å, $\beta = 91.64(1)°$, $Z = 4$, and $V = 2022.6(4)$ Å^3.*

Introduction

Recent work has shown that the 18-electron chlorocarbonyl complexes $MCl_2(CO)_2(PMe_3)_3$ (M = Mo, W) readily undergo alkylation at the metal center to afford the seven-coordinate species $MR(Cl)(CO)_2(PMe_3)_3$. In the large majority of the cases investigated, these alkyls have transient existence and experience a fast migratory insertion reaction with formation of the corresponding η^2-acyls $M(\eta^2\text{-}C(O)R)Cl(CO)(PMe_3)_3$.[2] In view of the current interest in hydride complexes of the transition metals,[3,4] and with the expectation that the well-known reduced migratory ability of H groups, as compared to alkyl functionalities, would allow the isolation of the primary hydride products, we have carried out the reactions of the above chloro complexes with the hydride reagent $LiBEt_3H$. In this contribution we report the results of this study, that includes the synthesis and structural characterization by spectroscopic techniques of the new compounds $MH(Cl)(CO)_2(PMe_3)_3$ (M = Mo (**2a**), W (**2b**)) as well as that of the related species $MH(X–X)(CO)_2(PMe_3)_2$ (X–X = anionic bidentate ligand). The molecular structure of the tungsten derivative **2b** has been determined by X-ray crystallography and is also reported.

Results and Discussion

The yellow compounds $MCl_2(CO)_2(PMe_3)_3$ (Mo (**1a**), W (**1b**)) undergo metathetical replacement of one of the chloride ligands by hydride upon reaction with $LiBEt_3H$. This transformation is best effected in Et_2O suspensions, in the presence of added PMe_3, and provides good yields of the novel, seven-coordinate hydride complexes $MH(Cl)(CO)_2(PMe_3)_3$ (M = Mo (**2a**), W (**2b**)), according to eq 1. Further metathesis to dihydride species does not take place, and in fact the use of more than 1 molar equiv of $LiBEt_3H$ causes an observable decrease in the yield of compounds **2**. Reaction 1 is very sensitive to the exact conditions and reagents used. For example $NaBH_4$ or H_2 does not furnish the desired compounds and employing tetrahydrofuran as the reaction solvent leads only to decomposition products. These observations are in common with those found in other hydride preparations.[3]

$$\underset{\mathbf{1a,b}}{MCl_2(CO)_2(PMe_3)_3} \xrightarrow[(PMe_3)]{LiBEt_3H} MHCl(CO)_2(PMe_3)_3 + LiCl + BEt_3 \quad (1)$$

M = Mo (**2a**), W (**2b**)

Compounds **2** are yellow, crystalline, air-sensitive solids. The presence of the hydride ligand confers them greater solubility in organic solvents, as compared to the parent dichlorides, but inferior thermal stability; their solutions decompose slowly at room temperature even under anaerobic and anhydrous conditions. Thus a solution of **2b** in C_6D_6 evolves H_2 completely at room temperature, over a period of 24 h, to give **1b** along with other unidentified species. This decomposition process must involve loss of PMe_3 at some stage since a considerable enhancement in the thermal stability of solutions of **2** is observed in the presence of added PMe_3.

Analytical and spectroscopic data for compounds **2** are in agreement with the proposed formulation. Their Nujol mull IR spectra display two strong bands in the range 1900–1800 cm^{-1} (ν_{C-O}), together with a medium intensity absorption at ca. 1875–1850 cm^{-1} attributable to the stretching of the M–H bond. In the IR solution spectra

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[2] (a) Carmona, E.; Contreras, L.; Poveda, M. L.; Sánchez, L. J.; Atwood, J. L.; Rogers, R. D. *Organometallics* **1991,** *10,* 61. (b) Carmona, E.; Contreras, L.; Gutiérrez-Puebla, E.; Monge, A.; Sánchez, L. J. *Organometallics* **1991,** *10,* 71.

[3] (a) Deutsch, P. P.; Eisenberg, R. *Chem. Rev.* **1988,** *88,* 1147. (b) Pearson, R. G. *Chem. Rev.* **1985,** *85,* 41. (c) Crabtree, R. H. In *Comprehensive Coordination Chemistry;* Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, U.K., 1987; Vol. II, Chapter 19.

[4] See for example: (a) Barthelat, J. C.; Chaudret, B.; Daudey, J. P.; De Loth, P.; Poilblanc, R. *J. Am. Chem. Soc.* **1991,** *113,* 9896. (b) Heinekey, D. M. *J. Am. Chem. Soc.* **1991,** *113,* 6074. (c) Van Der Zeijden, A. A. H.; Veghini, D.; Berke, H. *Inorg. Chem.* **1992,** *31,* 5106. (d) Van Der Zeijden, A. A. H.; Berke, H. *Helv. Chim. Acta* **1992,** *75,* 507. (e) Van Der Zeijden, A. A. H.; Bosch, H. W.; Berke, H. *Organometallics* **1992,** *11,* 2051. (f) Berry, A.; Green, M. L. H.; Bandy, J. A.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1991,** 2185. (g) Allen, D. A.; Green, M. L. H.; Bandy, J. A. *J. Chem. Soc., Dalton Trans.* **1990,** 541. (h) Van Der Sluys, L. S.; Eckert, J.; Eisenstein, O.; Hall, J. H.; Huffman, J. C.; Jackson, S. A.; Koetzle, T. F.; Kubas, G. J.; Vergamini, P. J.; Caulton, K. G. *J. Am. Chem. Soc.* **1990,** *112,* 4831. (i) Khalsa, G. R. K.; Kubas, G. J.; Unkefer, C. J.; Van Der Sluys, L. S.; Kubat-Martin, K. A. *J. Am. Chem. Soc.* **1990,** *112,* 3855.

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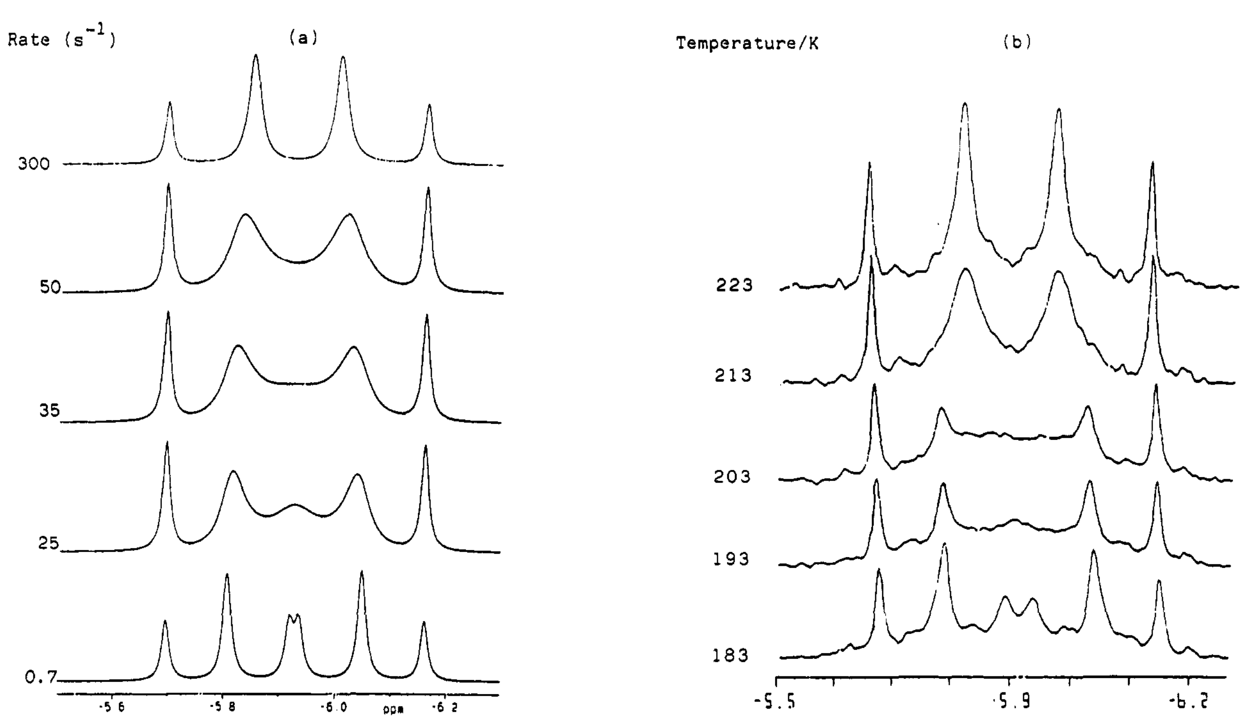

Figure 1. High field low-temperature ^{1}H NMR of the WH(Cl)(CO)$_2$(PMe$_3$)$_3$ complex: (a) simulated; (b) actual spectrum in CD$_3$COCD$_3$ (200 MHz).

this latter band can be found at 1830 and 1875 cm^{-1} for **2a** and **2b**, respectively.

NMR studies show the existence of only one species in the solutions of compounds **2** that undergoes a dynamic rearrangement involving mutual exchange of the phosphine groups as well as of the CO ligands. The presence of a M–H moiety is convincingly demonstrated by the observation, at room temperature, of a high field ^{1}H quartet centered at ca. −6 ppm. Figure 1 shows the appearance of the hydride resonance for **2b** in the temperature range from −90 to −50 °C. The low-temperature spectrum may be interpreted in terms of a doublet of triplets (or as a partially superimposed quartet of doublets) with the outer lines of the multiplet being appreciably sharper than the inner ones. Upon warming, the inner lines broaden but the outer ones remain sharp, with a constant separation of $^2J_{HP} + {}^2J_{HP'} + {}^2J_{HP''} = 92$ Hz. At −40 °C, the phosphine exchange process becomes fast and a binomial quartet with an average coupling of $^1/_3(^2J_{HP} + {}^2J_{HP'} + {}^2J_{HP''})$ is observed. Similar behavior has been reported for complexes undergoing related exchange phenomena.[5] The values of the $^2J_{HP}$ couplings computed from the −90 °C spectrum (ca. 47, 22, and 22 Hz) clearly indicate a transoid disposition of the hydride ligand with respect to one of the PMe$_3$ groups and cisoid to the other two. The hydride ligand is additionally coupled to ^{183}W ($^1J_{WH}$ ca. 20 Hz). This is a relatively small coupling since the one-bond J_{WH} constants are usually of the order of 35 Hz or higher.[6] Somewhat lower values have nevertheless been reported (e.g. between 25 and 30 Hz for WH(CO)$_2$NO(PR$_3$)$_2$ compounds,[7] 27 Hz for WH$_6$(PMe$_3$)$_3$ and WH$_4$(PMe$_3$)$_4$[8]), and extremely low couplings (of between 4 and 9 Hz) have been found recently by Templeton and co-workers in tris(pyrazolyl)borate complexes of tungsten[9a] and attributed to a low s-character of the W–H bond.

In agreement with the proposed ^{31}P site exchange, a relatively sharp singlet is observed in the ^{31}P{^{1}H} NMR spectra of **2a** and **2b** at δ −11.8 and −24.5, respectively. The ^{31}P–^{183}W coupling is retained in the fast-exchange limit, and this clearly demonstrates that the exchange process responsible for the equilibration of the PMe$_3$ ligands is intramolecular. As noted earlier, PMe$_3$ dissociation seems to be responsible for the low thermal stability of compounds **2**, but while this process may be of significance in the laboratory time scale it escapes undetected in the NMR time scale. Lowering the temperature to −90 °C (CD$_3$COCD$_3$) causes transformation of the ^{31}P{^{1}H} signal of **2b** into a triplet at ca. δ_x −29.6 ($^2J_{PP_x}$ = 20 Hz; $^1J_{P_xW}$ = 194 Hz) and a split AB quartet (δ_A −16.6; δ_B −21.7; $^2J_{AB}$ = 131 Hz; $^2J_{AX} = {}^2J_{BX}$ = 20 Hz; $^1J_{PW}$ = 209 and 216 Hz, respectively).

The room-temperature ^{13}C{^{1}H} NMR spectrum of **2a** shows a low field resonance at δ 218.1 assigned to the coordinated CO groups, that appears as a quartet due to coupling to the three ^{31}P nuclei. Interestingly, the corresponding signal of **2b** is a singlet flanked by tungsten satellites ($^1J_{CW}$ = 131 Hz), that becomes a doublet ($^2J_{CH}$ = 10 Hz) in the selective gated-decoupled spectrum. It is worth mentioning in this respect that the sign and magnitude of the two-bond X–X coupling constant depends markedly upon the X–M–X bond angle, with cis couplings being usually negative and of low absolute value and trans couplings generally positive and of higher magnitude.[9b] Accordingly, the lack of observation of ^{13}C–

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(5) Bars, O.; Braunstein, P.; Geoffroy, G. L.; Metz, B. *Organometallics* **1986**, *5*, 2021.

(6) (a) Piana, H.; Schubert, U. *J. Organomet. Chem.* **1991**, *411*, 303. (b) Alt, H. G.; Engelhardt, H. E.; Frister, T. *J. Organomet. Chem.* **1989**, *366*, 297.

(7) Carmona, E.; Contreras, L.; Daff, P. J.; Pizzano, A.; Sánchez, L. J. *Helv. Chim. Acta* **1992**, 407.

(8) Lyons, D.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1985**, 587.

(9) (a) Caffyn, A. J. M.; Feng, S. G.; Dierford, A.; Gamble, A. S.; Eldredge, P. A.; Vossen, M. R.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 2842. (b) Jameson, C. J. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1987; Chapter 6.3.5.

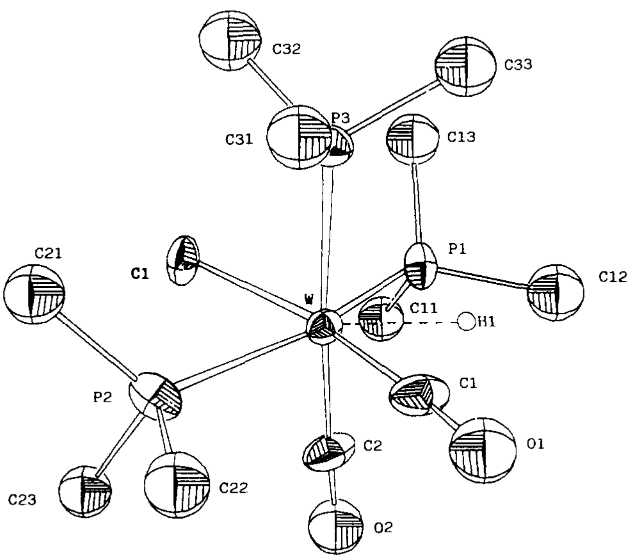
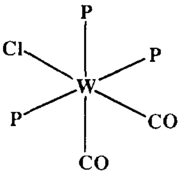


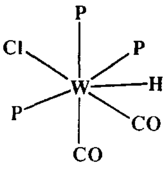
Figure 2. ORTEP drawing of **2b**.

^{31}P coupling at room temperature is likely due to a fortuitous cancelation of the coupling constants and, in accord with this assumption, there is appreciable line-broadening at lower temperatures and at -90 °C a doublet of triplets (δ 214.8, $^2J_{CP}$ = +45 and -22 Hz) and a quartet (δ 216.1, $^2J_{CP}$ = 6 Hz) are clearly discerned.

All these observations taken together unambiguously establish the presence in the molecules of compounds **2** of (i) a hydride ligand transoid with respect to one phosphine and cisoid to the others; (ii) three nonequivalent PMe_3 groups, two of them being mutually transoid, and (iii) two nonequivalent CO groups, one of them being transoid with respect to the unique PMe_3. If one ignores, for the time being, the hydride functionality, the octahedral distribution **A** can be proposed for the remaining ligands,



A

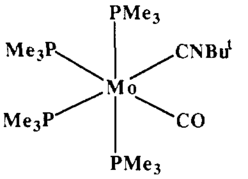


B

and this has been confirmed by a single crystal X-ray analysis, carried out with **2b**. These studies have allowed the location of the hydride ligand (see below) on one of the CO–P edges, as shown in **B**. The geometry of **2** can be approximately described as pentagonal bipyramidal. This is shown in Figure 2, which illustrates an ORTEP view of the molecules of this complex.

The coordination geometry of **2b** is similar to that found in other structurally characterized hydride complexes of Mo(II) and W(II), e.g. $MoH(BH_4)(PMe_3)_4$,[10a] $MoH(O_2CH)(PMe_3)_4$,[10b] $MoH(O_2CCF_3)(P(OMe)_3)_4$,[11a] and $WH(FBF_3)(CO)_3(PCy_3)_2$.[11b] It consists of PMe_3 and CO groups in the axial positions (C2–W–P3 angle of 176.9(5)°) and of two mutually transoid phosphines (P1–W–P2 = 158.5(1)°), one carbonyl, and the chloride and hydride ligands in the equatorial girdle. The equatorial donor atoms give an almost planar distribution (the W, Cl, C1 and H1 atoms are coplanar, while P1 and P2 deviate somewhat (0.18 and 0.15 Å, respectively) from this plane). The P1–W–H(1) angle of 57.3(1)° is similar to that encountered in $MoH_2(PMe_3)_5$ and $MoH(O_2CH)(PMe_3)_4$,[10b] while the larger P2–W–H1 angle of 142.7(1)° clearly corresponds to a transoid distribution of the phosphorus and hydrogen atoms, hence in excellent agreement with the conclusions of the NMR study discussed above. The two carbonyl–tungsten distances have normal values (W–C1 = 1.84(1), W–C2 = 1.89(1) Å), but the one corresponding to the CO ligand trans to the unique phosphine, i.e. W–C2, is appreciably longer than the other, in accord with the higher trans influence of the PMe_3 group as compared to the chloride ligand. Other bond distances and angles appear normal and compare well with those reported for related hydride complexes.[10,11]

In an attempt to obtain other analogous hydrides, the reaction of $MoCl_2(CN\text{-}t\text{-}Bu)CO(PMe_3)_3$ with $LiBEt_3H$ has been effected. A more complex transformation ensues in this case, the only isolable material being the Mo(0) species $Mo(CO)(CN\text{-}t\text{-}Bu)(PMe_3)_4$. Its IR spectrum shows two strong IR absorptions at 1780 and 1850 cm^{-1}, due respectively to ν(CO) and ν(CNR), while in its $^{31}P\{^1H\}$ NMR three resonances of relative intensity 1:1:2 are distinguishable. From this and other data collected in the Experimental Section, structure **C** can be proposed for this complex.



C

Although the second chloride ligand of compounds **2** cannot be replaced by a hydride, a facile metathesis reaction, which in addition entails the substitution of one of the PMe_3 ligands, takes place in the presence of anionic bidentate groups, with formation of the new hydrides **3–6** (eq 2). Compounds **3–6** are yellow crystalline solids that

$$\underset{\mathbf{2a,2b}}{\mathrm{MHCl(CO)_2(PMe_3)_3}} + \mathrm{M'(X{-}X)} \xrightarrow{-\mathrm{M'Cl},\ -\mathrm{PMe_3}} \mathrm{MH(X{-}X)(CO)_2(PMe_3)_2} \quad (2)$$

M = Mo, W

M′ = Na, K, or Tl

X–X = S_2CNMe_2 (**3a, 3b**), $S_2CO\text{-}i\text{-}Pr$ (**4a, 4b**), S_2COMe (**5b**), acac (**6b**)

can be handled in air for short periods of time but decompose readily upon longer exposures. They exhibit two strong IR absorptions due to the C–O stretching of

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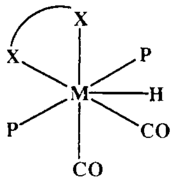
(10) (a) Atwood, J. L.; Hunter, W. E.; Carmona, E.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1980**, 467. (b) Lyons, D.; Wilkinson, G. Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1984**, 695.

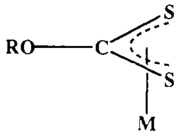
(11) (a) Wreford, S. S.; Kouba, J. K.; Kinner, J. F.; Muetterties, E. L.; Tavanaiepour, I.; Day, V. W. *J. Am. Chem. Soc.* **1980**, *102*, 1558. (b) Van der Sluys, L. S.; Kubat-Martin, K. A.; Kubas, G. J.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 306.

the coordinated CO groups, but no bands attributable to the hydride ligand can, in general, be found either in the Nujol mull or in the solution spectra. Unequivocal evidence for the presence of the M–H functionality can however be gathered by NMR spectroscopy.

The ^{1}H NMR spectra of **3–6** shows a high field triplet (δ ca. –5, $^2J_{HP} \sim 40$ Hz) fringed by tungsten satellites in the case of **3b–6b** ($^1J_{HW} \sim 16$–25 Hz). At –90 °C, the central line of the triplet splits into two, still somewhat broad, singlets, so that the overall pattern resembles a doublet of doublets ($^2J_{HP} = 64$ and 18 Hz, data for **3b**). The dynamic behavior exhibited by these complexes is also in accord with a mutual exchange process that interconverts the PMe_3 sites. The $^{31}P\{^1H\}$ NMR recorded at –90 °C is an AB quartet ($^2J_{AB} \sim 140$ Hz) that becomes a singlet at room temperature. From these data (see Experimental Section for some additional spectroscopic information) and by similarity with the geometry found for the parent hydrides **2**, structure **D** can be proposed for these complexes. It is worth noting in this respect that the ^{13}C resonance of the CS_2 group in the xanthates **4** and **5** displays coupling to the phosphorus atom ($^2J_{CP} \sim 11$ Hz) and to the hydride ligand ($^2J_{CH} \sim 9$ Hz). This can be taken in support of a trihapto, S, S′, C coordination mode for this ligand (structure **E**) as found recently in related Mo and W complexes.[12] In closing, it should also be mentioned that the acac derivative **6b** presents poor thermal stability and decomposes in solution with loss of the hydride ligand and formation of a red solid of analytical composition "W(acac)$(CO)_2(PMe_3)_2$". The structural characteristics of this compound have not been investigated any further.



D



E

Experimental Section

Microanalyses were carried out by Pascher Microanalytical Laboratory, Remagen (Germany), and by the Analytical Service of the University of Sevilla. $MCl_2(CO)_2(PMe_3)_3$ complexes (M = Mo, W) were synthesized as described previously.[13] Experimental conditions for manipulation of solvents and reagents and for preparative reactions can be found elsewhere.[2a]

IR spectra were recorded as Nujol mulls, or in an appropriate solvent, on a Perkin-Elmer 684 instrument. ^{1}H, ^{13}C, and ^{31}P NMR spectra were run on a Varian XL-200. ^{31}P NMR shifts were referenced to external 85% H_3PO_4, while ^{1}H and ^{13}C shifts were referenced respectively to the residual protio signal and ^{13}C resonance of the deuterated solvents employed.

The proton NMR spectrum in the high field region of **2b** was simulated by use of the DNMR4 program.[17]

Preparation of $MH(Cl)(CO)_2(PMe_3)_3$ (M = Mo (2a), W (2b)). $LiBEt_3H$ (6 mL of a 1 M THF solution, ca. 6 mmol) was placed via syringe into a 500-mL Schlenk flask filled with nitrogen and equipped with a magnetic stirring bar. The THF solvent was removed under vacuum before the addition of 200 mL of Et_2O, 3.24 g (ca. 6 mmol) of $WCl_2(CO)_2(PMe_3)_3$, and 0.5 mL of PMe_3. The resulting suspension was stirred for 3–5 h at room temperature and then centrifuged and evaporated to dryness. Crystallization of the residue from 200 mL of hexane at –25 °C afforded 1.22 g of yellow crystalline **2b**. A second crop of 0.46 g was obtained, giving a combined yield of ca. 55%. Starting with $MoCl_2(CO)_2(PMe_3)_3$ the complex $MoH(Cl)(CO)_2(PMe_3)_3$ was obtained in 45% yield by an analogous procedure.

$MoH(Cl)(CO)_2(PMe_3)_3$ (2a). Anal. Calcd for $C_{11}H_{28}O_2ClMo$: C, 32.63; H, 6.92. Found: C, 32.69; H, 6.98. IR (Nujol mull, cm^{-1}): 1905 (s), 1812 (s) (ν(CO)), 1855 (w) (ν(MoH)). ^{1}H NMR (20 °C, C_6D_6): δ 1.55 (m, PMe_3), –6.43 (q, $^2J_{HP} = 30.0$ Hz, Mo–H). $^{31}P\{^1H\}$ NMR (20 °C, C_6D_6): δ –11.8 (br s). $^{13}C\{^1H\}$ NMR (20 °C, C_6D_6): δ 18.7 (m, PMe_3), 218.1 (m, CO).

$WH(Cl)(CO)_2(PMe_3)_3$ (2b). Anal. Calcd for $C_{11}H_{28}O_2ClW$: C, 26.81; H, 5.96. Found: C, 26.75; H, 5.64. IR (Nujol mull, cm^{-1}): 1902 (s), 1806 (s) (ν(CO)), 1875 (w) (ν(WH)). ^{1}H NMR (20 °C, C_6D_6): δ –5.75 (q, $^2J_{HP} = 32.0$ Hz, $^1J_{HW} = 18.9$ Hz, W–H), 1.27 (m, PMe_3). ^{1}H NMR (–90 °C, CD_3COCD_3): δ –5.92 (dt, $^2J_{HP}$ = 49.6, 22.3 Hz, $^1J_{HW} = 19.5$ Hz, W–H), 1.38 (d, $^2J_{HP} = 6.8$ Hz, 1 PMe_3), 1.57 (filled-in doublet, $^2J_{HP} = 7.9$ Hz, 2 PMe_3). $^{31}P\{^1H\}$ NMR (20 °C, C_6D_6): δ –30.3 (br s, $^1J_{PW} = 207$ Hz). $^{31}P\{^1H\}$ NMR (–90 °C, CD_3COCD_3): δ ABX spin system $\upsilon_A = -16.6$, $\upsilon_B = -21.7$, $\upsilon_X = 29.6$ ($^2J_{P_AP_B} = 131$ Hz, $^2J_{P_ABP_X} = 21$ Hz, $^1J_{P_AW} = 209$ Hz, $^1J_{P_BW}$ = 216 Hz, $^1J_{P_XW} = 194$ Hz). $^{13}C\{^1H\}$ NMR (20 °C, C_6D_6): δ 19.2 (m, PMe_3), 214.7 (s, $^1J_{CW} = 131$ Hz, CO). $^{13}C\{^1H\}$ NMR (–90 °C, CD_3COCD_3): δ 17.3 (d, $^1J_{CP} = 24$ Hz, 1 PMe_3), 19.8 (d, $^1J_{CP}$ = 24 Hz, 2 PMe_3), 214.8 (dt, $^2J_{CP}$ = 45, 22 Hz, CO), 216.1 (q, $^2J_{CP}$ = 6 Hz, CO).

Attempted Reaction of $MoCl_2$(CN-*t*-Bu)CO$(PMe_3)_3$ and $LiBEt_3H$: Formation of Mo(CO)(CNBu^t)$(PMe_3)_4$. To a flask containing $MoCl_2$(CN-*t*-Bu)(CO)$(PMe_3)_3$ (0.25 g, 0.5 mmol) in 35 mL of Et_2O at room temperature was added $LiBEt_3H$ (0.5 mL of a 1 M THF solution, 0.5 mmol). The reaction mixture was stirred for 6 h before removal of the solvent in vacuum. The resulting yellow-orange solid was extracted and washed several times with petroleum ether, and the combined extracts were concentrated to ca. 10 mL. Centrifuging and cooling to –20 °C afforded Mo(CO)(CN-*t*-Bu)$(PMe_3)_4$ as yellow crystals in 25% yield.

Mo(CO)(CN-*t*-Bu)$(PMe_3)_4$ (7). Anal. Calcd for $C_{18}H_{45}NOP_4Mo$: C, 42.27; H, 8.80; N, 2.73. Found: C, 41.8; H, 9.2; N, 3.5. IR (Nujol mull, cm^{-1}): 1790 (s) (ν(CO)), 1870 (s) (ν(CN)). ^{1}H NMR (20 °C, C_6D_6): δ 1.12 (d, $^2J_{appHP} = 4.3$ Hz, 1 PMe_3), 1.24 (d, $^2J_{appHP} = 4.3$ Hz, 1 PMe_3), 1.48 (t, $^2J_{appHP} = 2.1$ Hz, 2 PMe_3), 1.29 (s, CMe_3). $^{31}P\{^1H\}$ NMR (20 °C, C_6D_6): δ –5.4 (dd, $^2J_{PP}$ = 26, 21 Hz, 2 PMe_3), –12.0 (dt, $^2J_{PP}$ = 29, 21 Hz, 1 PMe_3), –16.6 (dt, $^2J_{PP}$ = 29, 26 Hz, 1 PMe_3). $^{13}C\{^1H\}$ NMR (20 °C, C_6D_6): δ 23.7 (d, $^1J_{appCP} = 13$ Hz, 1 PMe_3), 25.2 (t, $^1J_{appCP}$ = 7 Hz, 2 PMe_3), 25.9 (d, $^2J_{appCP} = 14$ Hz, 1 PMe_3), 31.9 (s, $C\mathit{Me}_3$), 57.9 (s, $\mathit{C}Me_3$).

Preparation of MoH(X–X)$(CO)_2(PMe_3)_2$ Complexes. These complexes were prepared by treating the parent hydrides $MH(Cl)(CO)_2(PMe_3)_3$ (2) with appropriate salts of the corresponding bidentate ligands. The experimental procedure using the $MoH(S_2CNMe_2)(CO)_2(PMe_3)_2$ complex as a representative example, was as follows.

$MoH(S_2CNMe_2)(CO)_2(PMe_3)_2$ (3a). The salt NaS_2CNMe_2 (0.34 g, 2 mmol) was added to a yellow solution of $WH(Cl)(CO)_2(PMe_3)_3$ (0.50 g, 1 mmol) in THF (50 mL). The reaction mixture was stirred at room temperature for 24 h, during which time a pale orange color developed. The volume was then reduced in

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[12] (a) Carmona, E.; Galindo, A.; Gutiérrez-Puebla, E.; Monge, A.; Puerta, C. *Inorg. Chem.* **1986**, *25*, 3804. (b) Carmona, E.; Galindo, A.; Guille-Photin, C.; Laï, R.; Monge, A.; Ruiz, C.; Sánchez, L. *Inorg. Chem.* **1988**, *27*, 488.

[13] Carmona, E.; Doppert, K.; Marín, J. M.; Poveda, M. L.; Sánchez, L.; Sánchez-Delgado, R. *Inorg. Chem.* **1984**, *23*, 530.

[14] International Tables for X-Ray Crystallography; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, pp 72–98.

[15] Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

[16] Stewart, J. M. The XRAY 80 System. Computer Science Center, University of Maryland, College Park, 1985.

[17] Quantum Chemical Program Exchange, Indiana University, QCPE Program No. 466.

vacuo and the residue extracted with 15–20 mL of $\mathrm{Et_2O}$. After centrifugation and cooling at −20 °C complex **3a** was obtained as yellow-orange crystals in 80% yield.

Starting with the suitable $\mathrm{MH(Cl)(CO)_2(PMe_3)_3}$ complexes and the required bidentate ligand $\mathrm{NaS_2CNMe_2}$, $\mathrm{KS_2COR}$, or Tl(acac) led to the following compounds obtained by the above procedure: $\mathrm{WH(S_2CNMe_2)(CO)_2(PMe_3)_2}$ (**3b**) (70%), $\mathrm{MoH(S_2CO\text{-}\mathit{i}\text{-}Pr)(CO)_2(PMe_3)_2}$ (**4a**) (40%), $\mathrm{WH(S_2CO\text{-}\mathit{i}\text{-}Pr)(CO)_2(PMe_3)_2}$ (**4b**) (90%), $\mathrm{WH(S_2COMe)(CO)_2(PMe_3)_2}$ (**5b**) (25%), and $\mathrm{WH(acac)(CO)_2(PMe_3)_2}$ (**6b**) (42%).

Shorter reaction times (ca. 7 h) were however required for complexes **4a** and **6b**. They were all isolated as yellow-orange crystalline solids by cooling their concentrated petroleum ether solutions at temperatures of about −20 °C. The less soluble **3b** and **5b** complexes were crystallized from (1:1) petroleum ether–$\mathrm{Et_2O}$ solutions.

MoH(S$_2$CNMe$_2$)(CO)$_2$(PMe$_3$)$_2$ (3a). Anal. Calcd for $\mathrm{C_{11}H_{25}NO_2S_2P_2Mo}$: C, 31.06; H, 5.88; N, 3.29. Found: C, 31.73; H, 6.01; N, 3.34. IR (Nujol mull, cm^{-1}): 1897 (s), 1788 (s) (ν(CO)), 1834 (m) (ν(MoH)), 1497 (w) (ν(CN)). ^{1}H NMR (20 °C, $\mathrm{C_6D_6}$): δ −5.11 (t, $^2J_{\mathrm{HP}}$ = 39.4 Hz, Mo–H), 1.30 (t, $^2J_{\mathrm{appHP}}$ = 3.3 Hz, PMe$_3$), 2.68 (s, NMe$_2$). ^{31}P{^{1}H} NMR (20 °C, $\mathrm{C_6D_6}$): δ −3.7 (s). ^{13}C{^{1}H} NMR (20 °C, $\mathrm{C_6D_6}$): δ 16.8 (t, $^1J_{\mathrm{appCP}}$ = 12 Hz, PMe$_3$), 39.1 (s, NMe$_2$), 212.1 (s, S$_2$C), 226.0 (t, $^2J_{\mathrm{CP}}$ = 14 Hz, CO).

WH(S$_2$CNMe$_2$)(CO)$_2$(PMe$_3$)$_2$ (3b). Anal. Calcd for $\mathrm{C_{11}H_{25}NO_2S_2P_2W}$: C, 25.73; H, 4.87; N, 2.72. Found: C, 26.03; H, 5.41; N, 2.66. IR (Nujol mull, cm^{-1}): 1893 (s), 1784 (s) (ν(CO)), 1508 (w) (ν(CN)). ^{1}H NMR (20 °C, $\mathrm{C_6D_6}$): δ −4.90 (t, $^2J_{\mathrm{HP}}$ = 41.8 Hz, W–H), 1.39 (t, $^2J_{\mathrm{appHP}}$ = 3.7 Hz, PMe$_3$), 2.56 (s, NMe$_2$). ^{1}H NMR (−90 °C, $\mathrm{CD_3COCD_3}$): δ −5.43 (dd, $^2J_{\mathrm{HP}}$ = 64.1, 17.7 Hz, W–H), 1.42 (d, $^2J_{\mathrm{HP}}$ = 7.9 Hz, 1 PMe$_3$), 1.51 (d, $^2J_{\mathrm{HP}}$ = 8.5 Hz, 1 PMe$_3$), 1.60, 1.65 (br s, NMe$_2$). ^{31}P{^{1}H} NMR (20 °C, $\mathrm{C_6D_6}$): δ −21.4 (s, $^1J_{\mathrm{PW}}$ = 202 Hz). ^{31}P{^{1}H} NMR (−90 °C, $\mathrm{CD_3COCD_3}$): δ AB spin system ν_{A} = −9.7, ν_{B} = −17.4 ($^2J_{\mathrm{P_AP_B}}$ = 139 Hz, $^1J_{\mathrm{P_AW}}$ = 183 Hz, $^1J_{\mathrm{P_BW}}$ = 203 Hz). ^{13}C{^{1}H} NMR (20 °C, $\mathrm{CD_3COCD_3}$): δ 17.1 (t, $^1J_{\mathrm{appCP}}$ = 15 Hz, PMe$_3$), 39.7 (s, N*Me*$_2$), 213.6 (s, S$_2$C), 223.3 (t, $^2J_{\mathrm{CP}}$ = 11 Hz, $^1J_{\mathrm{CW}}$ = 138 Hz, CO). ^{13}C{^{1}H} NMR (−90 °C, $\mathrm{CD_3COCD_3}$): δ 14.7 (d, $^1J_{\mathrm{CP}}$ = 26 Hz, PMe$_3$), 17.3 (d, $^1J_{\mathrm{CP}}$ = 31 Hz, PMe$_3$), 39.9 (s, NMe$_2$), 212.4 (s, S$_2$C), 222.9 (t, $^2J_{\mathrm{CP}}$ = 11 Hz, $^1J_{\mathrm{CW}}$ = 142 Hz, CO).

MoH(S$_2$CO-*i*-Pr)(CO)$_2$(PMe$_3$)$_2$ (4a). Anal. Calcd for $\mathrm{C_{12}H_{26}O_3S_2P_2Mo}$: C, 32.73; H, 5.91. Found: C, 32.98; H, 5.72. IR (Nujol mull, cm^{-1}): 1916 (s), 1810 (s) (ν(CO)). ^{1}H NMR (20 °C, $\mathrm{C_6D_6}$): δ −5.23 (t, $^2J_{\mathrm{HP}}$ = 38.7 Hz, Mo–H), 1.20 (t, $^2J_{\mathrm{appHP}}$ = 3.6 Hz, PMe$_3$), 1.45 (d, $^3J_{\mathrm{HH}}$ = 6.1 Hz, CH*Me*$_2$), 5.37 (h, *C*HMe$_2$). ^{31}P{^{1}H} NMR (20 °C, $\mathrm{C_6D_6}$): δ −2.4 (s). ^{13}C{^{1}H} NMR (20 °C, $\mathrm{CD_3COCD_3}$): δ 17.4 (t, $^1J_{\mathrm{appCP}}$ = 13 Hz, PMe$_3$), 21.8 (s, CH*Me*$_2$), 76.2 (s, *C*HMe$_2$), 225.4 (t, $^2J_{\mathrm{CP}}$ = 14 Hz, CO), 227.1 (br s, S$_2$C).

WH(S$_2$CO-*i*-Pr)(CO)$_2$(PMe$_3$)$_2$ (4b). Anal. Calcd for $\mathrm{C_{12}H_{26}O_3S_2P_2W}$: C, 27.27; H, 4.92. Found: C, 28.05; H, 5.15. IR (Nujol mull, cm^{-1}): 1914 (s), 1806 (s) (ν(CO)). 1850 (w) (ν(WH)). ^{1}H NMR (20 °C, $\mathrm{C_6D_6}$): δ −5.12 (t, $^2J_{\mathrm{HP}}$ = 41.3 Hz, $^1J_{\mathrm{HW}}$ = 25.5 Hz, W–H), 1.05 (d, $^3J_{\mathrm{HH}}$ = 6.1 Hz, CH*Me*$_2$), 1.29 (t, $^2J_{\mathrm{appHP}}$ = 3.9 Hz, PMe$_3$), 5.28 (h, *C*HMe$_2$). ^{31}P{^{1}H} NMR (20 °C, $\mathrm{C_6D_6}$): δ −19.9 (s, $^1J_{\mathrm{PW}}$ = 202 Hz). ^{13}C{^{1}H} NMR (20 °C, $\mathrm{C_6D_6}$): δ 16.9 (t, $^1J_{\mathrm{appCP}}$ = 15 Hz, PMe$_3$), 21.2 (s, CH*Me*$_2$), 74.7 (s, *C*HMe$_2$), 219.6 (t, $^2J_{\mathrm{CP}}$ = 11 Hz, CO), 228.0 (t, $^2J_{\mathrm{CP}}$ = 7 Hz, S$_2$C).

WH(S$_2$COMe)(CO)$_2$(PMe$_3$)$_2$ (5b). Anal. Calcd for $\mathrm{C_{10}H_{22}O_3S_2P_2W}$: C, 24.00; H, 4.40. Found: C, 24.71; H, 4.63. IR (Nujol mull, cm^{-1}): 1905 (s), 1804 (s) (ν(CO)). ^{1}H NMR (20 °C, $\mathrm{C_6D_6}$): δ −5.15 (t, $^2J_{\mathrm{HP}}$ = 42.4 Hz, $^1J_{\mathrm{HW}}$ = 23.8 Hz, W–H), 1.24 (t, $^2J_{\mathrm{appHP}}$ = 3.7 Hz, PMe$_3$), 3.46 (s, OMe). ^{31}P{^{1}H} NMR (20 °C, $\mathrm{C_6D_6}$): δ −20.3 (s, $^1J_{\mathrm{PW}}$ = 202 Hz). ^{13}C{^{1}H} NMR (20 °C, THF): δ 16.3 (t, $^1J_{\mathrm{appCP}}$ = 15 Hz, PMe$_3$), 56.8 (s, OMe), 219.0 (t, $^2J_{\mathrm{CP}}$ = 11 Hz, CO), 229.0 (t, $^2J_{\mathrm{CP}}$ = 7 Hz, S$_2$C). ^{13}C gated (20 °C, THF): δ 219.0 (td, $^2J_{\mathrm{CH}}$ = 9 Hz, CO), 229.0 (td, $^2J_{\mathrm{CH}}$ = 11 Hz, S$_2$*C*).

WH(acac)(CO)$_2$(PMe$_3$)$_2$ (6b). Anal. Calcd for $\mathrm{C_{13}H_{26}O_4P_2W}$: C, 31.70; H, 5.28. Found: C, 31.87; H, 5.11. IR (Nujol mull, cm^{-1}): 1890 (s), 1862 (s), 1781 (s) (ν(CO)), 1568 (m), 1516 (m) (ν(CO) acac). IR (petroleum ether solution, cm^{-1}): 1912 (s), 1838 (s) (ν(CO)), 1817 (w) (ν(WH)), 1578 (ν(CO) acac). ^{1}H NMR (20 °C, $\mathrm{C_6D_6}$): δ −3.27 (t, $^2J_{\mathrm{HP}}$ = 33.1 Hz, $^1J_{\mathrm{HW}}$ = 16.2 Hz, W–H), 1.06 (t, $^2J_{\mathrm{appHP}}$ = 3.5 Hz, PMe$_3$) 1.68 (s, OCCH$_3$), 5.05 (s, CH). ^{31}P{^{1}H} NMR (20 °C, $\mathrm{C_6D_6}$): δ −7.8 (s, $^1J_{\mathrm{PW}}$ = 247 Hz). ^{13}C{^{1}H} NMR (20 °C, $\mathrm{C_6D_6}$): δ 15.8 (t, $^1J_{\mathrm{appCP}}$ = 13 Hz, PMe$_3$), 26.9 (s, OC*C*H$_3$), 100.9 (s, CH), 187.1 (s, O*C*CH$_3$), 226.7 (br s, CO). ^{13}C{^{1}H} NMR (−90 °C, $\mathrm{CD_3COCD_3}$): δ 15.6 (t, $^1J_{\mathrm{CPapp}}$ = 13 Hz, PMe$_3$), 27.6 (s, OC*C*H$_3$), 102.5 (s, CH), 188.7 (s, O*C*CH$_3$), 227.8 (t, $^2J_{\mathrm{CP}}$ = 10 Hz, CO).

Table I. Crystallographic Data for 2b

formula	$\mathrm{WClP_3O_2C_{11}H_{28}}$	Z	4
fw	504.6	D_{calc}, g cm^{-3}	1.66
space group	$P2_1/c$	μ(Mo Kα)	62.0
a, Å	14.514(1)	T, °C	22
b, Å	8.471(7)	λ, cm^{-1}	0.710 69
c, Å	16.458(3)	R	0.039
β, deg	91.64(1)	R_{w}	0.041
V, Å^3	2022.6(4)		

Table II. Final Atomic Parameters of 2b

atom	x/a	y/b	z/c	U_{eq},[a] Å^2
W	0.77933(3)	0.43136(6)	0.83694(3)	510(1)
Cl	0.66996(22)	0.20896(37)	0.80467(22)	786(12)
P1	0.64921(25)	0.58205(42)	0.77540(21)	734(12)
P2	0.88138(25)	0.19926(52)	0.86897(21)	793(14)
P3	0.72175(24)	0.44000(54)	0.97987(19)	796(13)
O1	0.94421(91)	0.64562(163)	0.87974(79)	1410(45)
O2	0.85508(81)	0.44573(163)	0.66440(74)	1312(39)
C1	0.87622(89)	0.56409(208)	0.86279(81)	940(58)
C2	0.82539(98)	0.43569(206)	0.73059(78)	967(59)
C11	0.61550(109)	0.52375(202)	0.67260(97)	1099(52)
C12	0.66592(144)	0.79213(273)	0.76216(127)	1556(78)
C13	0.53856(122)	0.57433(246)	0.82079(107)	1314(61)
C21	0.84165(115)	0.04711(228)	0.93857(103)	1214(56)
C22	0.99541(128)	0.24359(236)	0.90730(112)	1329(64)
C23	0.90430(101)	0.08441(203)	0.78096(89)	1020(46)
C31	0.80440(121)	0.40809(233)	1.06214(106)	1279(60)
C32	0.62996(132)	0.30608(251)	1.00730(117)	1396(68)
C33	0.67269(134)	0.62560(244)	1.01358(118)	1411(71)

[a] $U_{\mathrm{eq}} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

Table III. Selected Bond Distances (Å) and Angles (deg) for 2b

W–H1	1.78	W–C1	1.84(1)
W–Cl	2.510(3)	W–C2	1.89(1)
W–P1	2.472(4)	O1–C1	1.23(2)
W–P2	2.509(4)	O2–C2	1.19(2)
W–P3	2.520(3)		
C1–W–C2	85.1(6)	Cl–W–P3	89.7(1)
P3–W–C2	176.9(5)	Cl–W–P2	79.8(1)
P3–W–C1	92.1(4)	Cl–W–P1	80.2(1)
P2–W–C2	89.3(5)	W–C1–O1	176(1)
P2–W–C1	89.3(4)	W–C2–O2	177(2)
P2–W–P3	92.0(1)	H1–W–C2	86.0(4)
P1–W–C2	84.1(4)	H1–W–C1	53.5(5)
P1–W–C1	110.5(6)	H1–W–P3	91.27(8)
P1–W–P3	95.6(1)	H1–W–P2	142.70(9)
P1–W–P2	158.5(1)	H1–W–P1	57.32(9)
Cl–W–C2	93.3(4)	H1–W–Cl	137.41(8)
Cl–W–Cl	168.9(5)		

X-ray Structure Determinations. A summary of the crystal data is given in Table I. Final atomic parameters and selected bond distances and angles are given in Tables II and III, respectively. A yellow prism of approximate dimensions 0.08 × 0.12 × 0.06 mm was coated with an Epoxy resin and mounted on a Enraf-Nonius CAD 4 diffractometer. The cell dimensions were refined by least-squares fitting the values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for W, P, and Cl were taken from ref 14. The structure was solved by Patterson and Fourier methods. An empirical absorption correction was applied at the end of the isotropic refinement.[15] The C atoms of the methyl groups were refined isotropically because of some unresolvable disorder from the thermal motion. After several cycles of mixed refinement the H1 atom was located in a difference synthesis as the highest peak of the map with 0.7 e Å^{-3}. No trend in ΔF versus F_{o} or $(\sin\theta)/\lambda$

was observed. Final refinement was fixed isotropic factors and coordinates for H atoms led to $R = 3.9$ and $R_w = 4.1$.

Most of the calculations were carried out with the XRAY 80 system.[16]

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Supplementary Material Available: Tables of H atom coordinates and thermal parameters for **2b** (2 pages). Ordering information is given on any current masthead page.

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