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Bis(ethylene) complexes of molybdenum- and tungsten-(0) containing the $CH_3C(CH_2PMe_2)_3$ ligand: synthesis, solution conformation and reactivity

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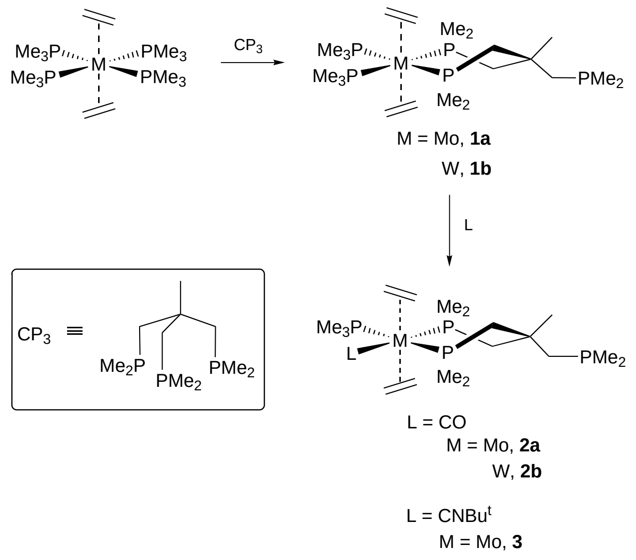
The reaction of *trans*-$[M(C_2H_4)_2(PMe_3)_4]$ with the tripodal phosphine 1,1,1-tris[(dimethylphosphino)methyl]-ethane (CP_3) affords complexes *trans*-$[M(C_2H_4)_2(\eta^2\text{-}CP_3)(PMe_3)_2]$ (M = Mo **1a** or W **1b**). A detailed NMR study, including hetero- and homo-nuclear two-dimensional correlations, has been carried out for **1b** which allows a complete assignment of signals and a structural spectroscopic determination. In solution, no ethylene rotation is observed at room temperature and the preferential conformer of the six-membered ring $W[\eta^2\text{-}CH_3C(CH_2PMe_2)_3]$ fragment is, on the basis of steric arguments, the skew-boat conformation. Interaction of compounds **1** with CO affords *trans*-$[M(C_2H_4)_2(\eta^2\text{-}CP_3)(CO)(PMe_3)]$ (M = Mo **2a** or W **2b**), while reaction of **1a** with $CNBu^t$ furnishes the compound *trans*-$[Mo(C_2H_4)_2(\eta^2\text{-}CP_3)(CNBu^t)(PMe_3)]$ **3**. The bidentate co-ordination of CP_3 induces chirality at the metal center and compounds **2** and **3** are obtained as a *ca.* 1 : 1 mixture of diastereoisomers, identified by the presence of two different patterns of resonances in their $^{31}P\text{-}\{^1H\}$ NMR spectra at low temperature. At the fast regimen exchange, the isomers are interconverted through bis(ethylene) rotation. A variable-temperature $^{31}P\text{-}\{^1H\}$ NMR study carried out for **2a** gives an approximate value of $\Delta G^‡$ for this process of 55 kJ mol^{-1} at 298 K.

The use of chelating polydentate phosphine ligands in co-ordination and organometallic chemistry is quite widespread and widely exploited.[1] This is an area of much current interest because of its potential advantageous applications, particularly in homogeneous catalysis and catalytic asymmetric synthesis,[2] as compared to monodentate ligands.

In the past few years, the synthesis and chemical reactivity of the bis(ethylene) complexes[3] *trans*-$[M(C_2H_4)_2(PMe_3)_4]$ (M = Mo or W) have been studied in our laboratories, in particular their interaction with carbon dioxide[4] and other heteroallenes.[5] Recently, we have reported bis(ethylene) complexes of Mo^0 and W^0 containing bidentate phosphines[6] and phosphites.[7] As a continuation of this work we have now enlarged the range of bis(ethylene) complexes of these metals using the tripodal phosphine 1,1,1-tris[(dimethylphosphino)methyl]ethane [$CH_3C(CH_2PMe_2)_3$, CP_3].[8] Here we wish to report the synthesis and characterization of novel bis(ethylene) complexes containing the CP_3 phosphine co-ordinated in a η^2 fashion, namely *trans*-$[M(C_2H_4)_2(\eta^2\text{-}CP_3)(PMe_3)_2]$ (M = Mo **1a** or W **1b**). Detailed homo- and hetero-nuclear two-dimensional NMR studies on the tungsten derivative, as well as the interaction of **1** with CO or $CNBu^t$ to produce *trans*-$[M(C_2H_4)_2(\eta^2\text{-}CP_3)(L)(PMe_3)]$ (L = CO **2** or $CNBu^t$ **3**) are also reported.



Scheme 1

Results and Discussion

Synthesis and spectroscopic properties of *trans*-$[M(C_2H_4)_2(\eta^2\text{-}CP_3)(PMe_3)_2]$ [M = Mo 1a or W 1b, $CP_3 = CH_3C(CH_2PMe_2)_3$]

Stable zerovalent Group 6 *cis*-bis(ethylene) complexes are not known;[9] since in an octahedral complex containing a co-ordinated tripodal *fac*-phosphine the remaining co-ordination sites are necessarily in an all-*cis* disposition, we planned the synthesis of *cis*-bis(ethylene) derivatives through PMe_3 substitution by a tripodal phosphine (CP_3) in *trans*-$[M(C_2H_4)_2(PMe_3)_4]$ (M = Mo or W). However, light petroleum solutions of *trans*-$[M(C_2H_4)_2(PMe_3)_4]$ complexes react with CP_3 at room temperature with displacement of only two PMe_3 ligands and formation of the compounds *trans*-$[M(C_2H_4)_2(\eta^2\text{-}CP_3)(PMe_3)_2]$ **1** (Scheme 1). No other metal–CP_3 products were observed during the course of the reaction by $^{31}P\text{-}\{^1H\}$ NMR, the reaction being essentially quantitative. Heating solutions of **1**, in order to transform the η^2 co-ordination mode of the CP_3 ligand to the classical tripodal η^3 one, produces only intractable products.

Compounds **1** are pale yellow crystalline solids, very soluble in light petroleum and other non-polar solvents and air sensitive, particularly in solution. Their IR spectra display the characteristic absorptions for the ethylene groups and bands corresponding to the phosphine ligands. The $^{31}P\text{-}\{^1H\}$ NMR spectra consist of four doublets of triplets for the phosphorus nuclei co-ordinated to the metal atom and one singlet at high field (δ −62.5 **1a**, −64.1 **1b**). The latter are assigned to a non-co-ordinated phosphorus atom which confirms the bidentate co-ordination[10] of the tripodal-phosphine.[‡] The $^{31}P\text{-}\{^1H\}\text{–}^{31}P\text{-}\{^1H\}$ homonuclear and $^{31}P\text{-}\{^1H\}\text{–}^1H$ heteronuclear NMR

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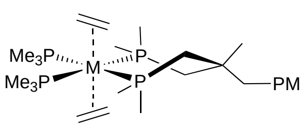
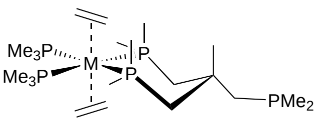
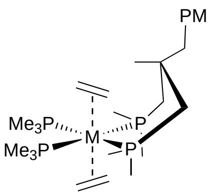
[‡] Selected examples of η^2-tripod-phosphine ligands are given in ref. 11.



Ia



Ib



Ic

correlations allowed us to distinguish the signals caused by the PMe_3 ligands and the PMe_2 fragments. Unlike other bis(ethylene) complexes of Mo and W with bidentate phosphines, whose NMR spectra are in agreement with the existence of a C_2 symmetry axis located in the plane that contains the four P atoms,[6,12] the $^{31}P-\{^1H\}$ NMR spectroscopic data for **1** suggest a lack of elements of symmetry. The carbon atoms of the ethylene ligands generate four different signals in the $^{13}C-\{^1H\}$ spectra, in the range δ 25–27 (**1a**) or 16–18 (**1b**), indicating that ethylene rotation is not taking place at room temperature.

The six-membered ring of the $M[\eta^2-CH_3C(CH_2PMe_2)_3]$ fragment in compounds **1** can adopt three possible conformations, namely skew-boat, chair and boat, as shown in **Ia**, **Ib** and **Ic** respectively. Although a systematic structural conformational analysis[13] has appeared for the five-membered ring $M(Ph_2PCH_2CH_2PPh_2)$, no similar studies, to our knowledge, have been performed with a six-membered ring of a bidentate phosphine.§ However, the conformational analysis of related six-membered metal–diamine chelate rings has been performed,[15] and, although six-membered metallacycles are rather flexible,¶ these analyses show that the chair conformation represents the minimum energy geometry. The steric repulsions found in these derivatives between the axial positions of the ring and the apical *cis* coligands are the major repulsive interactions and, thus, the boat conformation is the most destabilized. In the solid state, the boat disposition of a six-membered ring bidentate tripod ligand has been observed in some planar ML_4 compounds.[17] Conversely, the other two conformers, chair and skew-boat, have been both authenticated in several η^2-tripod-phosphine derivatives.[10,11d,11g,18]

The ethylene ligands in compounds **1** occupy the characteristic *trans* positions with an eclipsed-perpendicular geometrical disposition.|| No ethylene rotation is observed at room temperature and, consequently, this rigid conformation generates different steric interactions with the distinct axial positions of the six-membered ring. Intuitively, the repulsive interactions between the hydrogen atoms of the ethylene ligands and the axial methyl substituents of the PMe_2 groups for the chair conformer are greater than the same interactions for the skew-boat (see **I**). Molecular models, built for both isomers,** clearly show higher steric repulsions for the chair isomer than for the skew-boat one. Taking into account all these facts, we propose the latter conformation (**Ia**) as the preferential conformer of the six-membered chelate ring $M[\eta^2-CH_3C(CH_2PMe_2)_3]$ in solution.

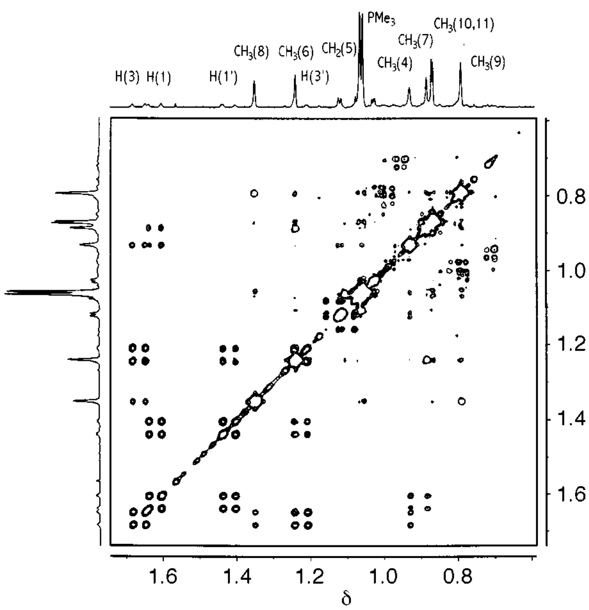
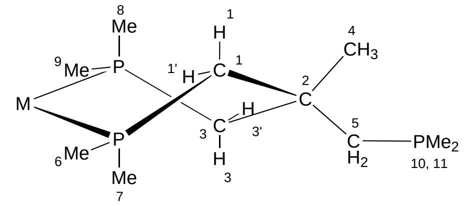


Fig. 1 The $^1H-^1H-\{^{31}P\}$ two-dimensional correlation (COSY) spectrum of *trans*-$[W(C_2H_4)_2(\eta^2-CP_3)(PMe_3)_2]$ **1b**



II

A complete assignment of the CP_3 phosphine signals in the ^1H and ^{13}C NMR spectra for the complex **1b** was made through two-dimensional hetero- and homo-nuclear NMR techniques. We made use of the Kraihanzel approach,[20] that applies the concepts used in the analysis of the spectra of substituted cyclohexanes, to assign the ^1H and $^{13}C-\{^1H\}$ signals of complex **1b** and by comparison to those of the molybdenum derivative. The following discussion is based on the numbering scheme of **II**.

The ^1H NMR spectrum of **1b** is typified by the presence of nine different methyl signals. The assignment is made on the basis of the $^{31}P-\{^1H\}-^1H$ heteronuclear NMR correlation. Four signals are originated by the methyl groups of the two coordinated PMe_2 fragments at δ 1.35, $CH_3(8)$; 1.24, $CH_3(6)$; 0.89, $CH_3(7)$; and 0.80, $CH_3(9)$. Two resonances at δ 1.06 and 1.05 are due to the two inequivalent PMe_3 ligands and the methyl groups of the PMe_2 pendant arm give two doublets at δ 0.87 and 0.86. The singlet at δ 0.93 is due to the C-methyl group. The hydrogen nuclei of the methylene units of the ring are diastereotopic and exhibit four different signals at δ 1.66, H(3); 1.62, H(1); 1.41, H(1′); 1.22, H(3′). Geminal coupling constants of $^2J[H(1)-H(1')] = 13$ and $^2J[H(3)-H(3')] = 14$ Hz were observed in the $^1H-\{^{31}P\}$ NMR spectrum. The remaining resonances are due to the ethylene protons and they are partially obscured by the P–Me absorptions. The assignment and location of the hydrogen atoms on the CP_3 fragment were confirmed by $^1H-^1H$ and $^1H-^{13}C-\{^1H\}$ correlations and were based upon a preferential skew-boat configuration of the six-membered chelate ring. Fig. 1 shows the COSY phosphorus decoupled spectrum of **1b**. The H(3) proton signals are related to the geminal H(3′), the C-methyl(4) and the Me(8) resonances, while H(1) correlates with the corresponding geminal H(1′), the C-methyl(4) and the Me(7) absorptions. This trend compares well with the empirical rule of coplanar coupling through four-bonds (*M* or *W* type).[20] Conversely, the H(3′) and H(1′) signals are only related to the respective geminal protons H(3) and H(1) and with each other. Both facts are in agreement with an assignment of axial

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§ Recently, a conformational analysis of η^3-tripod cobalt templates has been reported in ref. 14.

¶ Different conformations have been found recently in the same crystal in ref. 16.

|| This structural conformation has been authenticated experimentally[3,6,7] and studied theoretically.[19]

** Selected bond distances and angles have been taken from the Cambridge Structural Database to mimic the two conformations.

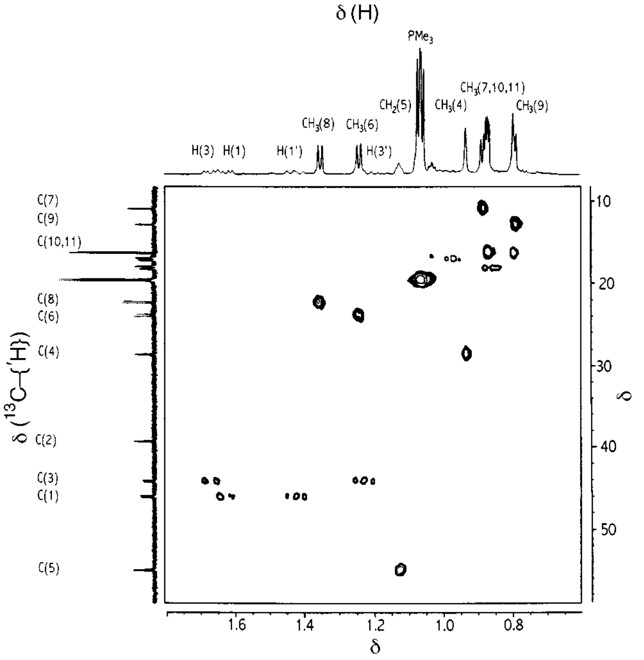


Fig. 2 The ^1H–^{13}C-{^1H} spectrum of *trans*-[$W(C_2H_4)_2(\eta^2\text{-}CP_3)(PMe_3)_2$] **1b**

positions for the hydrogen atoms 1 and 3, and equatorial for 1′ and 3′.

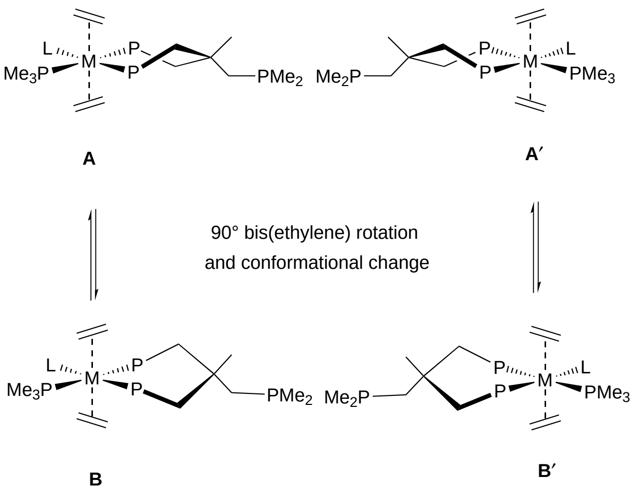
The ^{13}C-{^1H} NMR spectrum of **1b** consists of seventeen signals, two doublets corresponding to the two PMe_3 ligands, four multiplets in the range δ 16–18 to the bis(ethylene) fragment and eleven absorptions for the carbon atoms of the skeleton of the CP_3 phosphine. The methyl groups of the PMe_2 co-ordinated fragments show doublets centered at δ 10.7 C(7), 12.6 C(9), 22.1 C(8) and 23.7 C(6), where the assignments have been made through the ^1H–^{13}C-{^1H} two-dimensional NMR spectrum displayed in Fig. 2. In the same way, the three methylene signals that appear at low field, one as a doublet of triplets and the other two as doublets of doublets are assigned to C(5), C(1) and C(3), respectively. Finally, the quaternary carbon atom and the methyl group bonded to it appear as doublets of triplets at δ 39.1 and 28.4, respectively.

Reactions of compounds 1 with CO and CNBu^t: *trans*-[$M(C_2H_4)_2(\eta^2\text{-}CP_3)(L)(PMe_3)$] (L = CO 2 or CNBu^t 3)

When solutions of compounds **1** are pressurized with carbon monoxide (2 atm, 1 atm = 101 325 Pa, room temperature), substitution of one of the PMe_3 groups by CO is observed with formation of complexes **2** in good yield. In a similar way, addition of 1 equivalent of CNBu^t to a solution of compound **1a** in light petroleum, leads to the molybdenum derivative *trans*-[$Mo(C_2H_4)_2(\eta^2\text{-}CP_3)(CNBu^t)(PMe_3)$] **3** (Scheme 1). Complexes **2** and **3** are pale yellow and yellow crystalline materials, very soluble in light petroleum and other non-polar solvents. They are air sensitive in the solid state and decompose readily in solution upon exposure to air.

The co-ordination of CO to the metal center is confirmed by inspection of the IR spectra (Nujol) which exhibit a broad absorption around 1840 cm^{-1}, characteristic of a strong interaction between the metal and the CO molecule. Also, in the case of the compound **3**, a broad intense absorption at 1970 cm^{-1} is indicative of the co-ordination of the isonitrile. In both cases, the values of ν(CO) and ν(CN) compare well with those reported for *trans*-[$M(C_2H_4)_2(L)(PMe_3)_3$] complexes.[3,21]

The ^1H and ^{13}C-{^1H} NMR spectra of these compounds are not very informative. Noteworthy, they exhibit broad bands typical of a fluxional behavior in contrast to the spectra of the parent compounds **1**. The ^{31}P-{^1H} NMR spectra of **2** and **3** change with temperature. A variable-temperature ^{31}P-{^1H} NMR (125 MHz, [$^2H_8$]toluene) study was carried out for **2a**. At 323 K, the spectrum reveals three resonances due to one AMX spin system (centered at δ 1.6, PMe_2; −6.4, PMe_3 and −14.2, PMe_2) and one singlet (δ −69.3, non-co-ordinated PMe_2) in conformity with the presence of only one species in solution which possesses no equivalent phosphorus atoms. Cooling of the sample leads to considerable line broadening, except for the characteristic resonances of the PMe_3 ligands which only show a slight low-field chemical shift displacement. At 253 K, in the limit of the slow interchange, the presence of two AMX spin systems in the ^{31}P-{^1H} NMR spectrum is indicative of the existence of two isomers in an approximately 1 : 1 ratio. The isomers display phosphorus resonances at δ 2.1, −5.2, −12.7 and −70.1 (species A) and signals at δ 0.8, −5.1, −15.6 and −70.4 (species B). Both species have approximately equal values for the J(P–P) coupling constants with no variation in magnitude with temperature. This fact, together with the similar chemical shifts, is indicative of two chemically and structurally very similar species.



Scheme 2

Scheme 2 illustrates an interpretation for these results. Species A and B differ in the orientation of the ethylene molecules and in the δ- and λ-skew-boat conformation of the chelate ring.

Species A and B are diastereoisomers giving different signals in the NMR spectrum as is observed in the slow interchange region (species labeled A′ and B′ are the respective enantiomers). An increase in temperature favors the metal–olefin rotation and produces the interconversion of the isomers. This interconversion proceeds through concerted conrotatory motion of the two C_2H_4 ligands and simultaneous change in the δ- and λ-skew-boat conformations of the six-membered chelate ring (see Scheme 2). This process originates the observation of the average spectrum in the fast interchange limit. A conrotatory mechanism for *trans*-bis(alkene) rotation has been proposed recently in Mo^0 complexes,[22] analogous to that reported for *trans*-bis(carbon dioxide) rotation in Mo^0 derivatives.[23] Line-shape analysis of the variable-temperature ^{31}P-{^1H} NMR spectra of **2a** was carried out (see Experimental section) and Fig. 3 shows an example of experimental and simulated spectra. The slope and intercept of an Eyring plot[24] (see Fig. 4) yields the following approximate values for the activation parameters: $\Delta H^{\ddagger} = 83$ kJ mol^{-1}, $\Delta S^{\ddagger} = 93$ J mol^{-1} K^{-1}. Application of the Eyring equation gives an approximate value of $\Delta G^{\ddagger} = 55$ kJ mol^{-1} at 298 K for the barrier to interconversion of the diastereoisomers. This value for the $\Delta G^{\ddagger}$ rotation barrier is smaller than those reported for the bis(olefin) compounds *trans*-[$Mo(C_2H_4)_2(dppe)_2$] (estimated at 64.1 kJ mol^{-1}, dppe = $Ph_2PCH_2CH_2PPh_2$)[25] and [$W(\eta^2\text{-}H_2C{=}CHCO_2Me)_2(CO)_4$] (75.4 kJ mol^{-1})[26] but higher than the recently reported

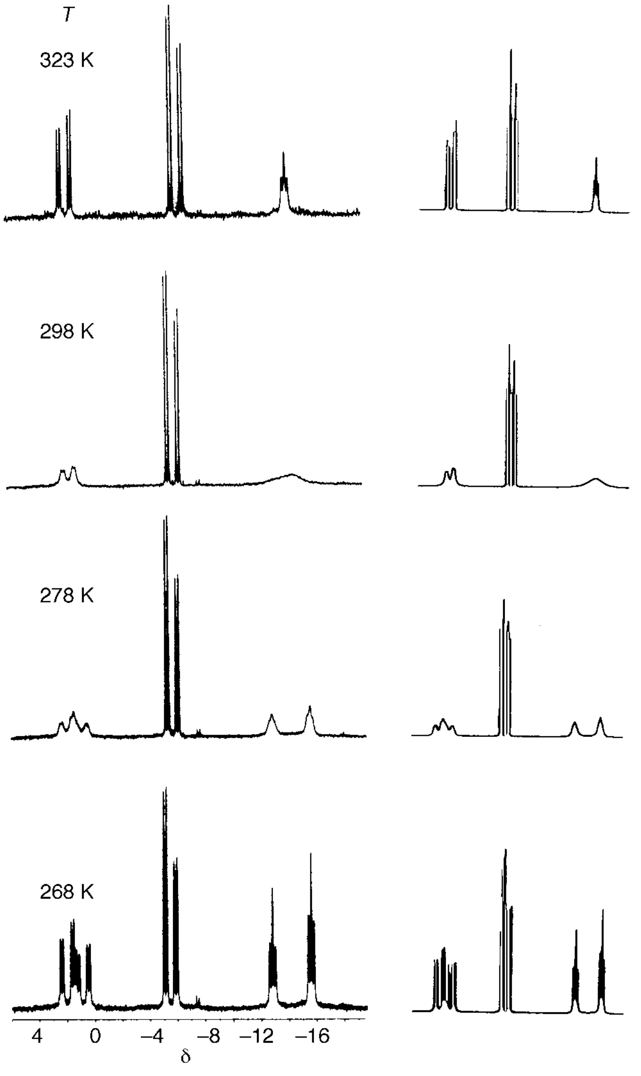


Fig. 3 The ^{31}P-{^1H} variable-temperature NMR spectra of complex $[Mo(C_2H_4)_2(\eta^2\text{-}CP_3)(CO)(PMe_3)]$ **2a**. Left: experimental, right: computer-simulated spectra

values for several *trans*-$[W(\eta^2\text{-alkene})_2(CO)_4]$ complexes (38.8–48.5 kJ mol^{-1}).[27]

Heating the compound *trans*-$[Mo(C_2H_4)_2(\eta^2\text{-}CP_3)(CO)(PMe_3)]$ at 80 °C produces the co-ordination of the phosphorus atom of the pendant arm of the tripod-phosphine and the release of an ethylene molecule. The change of the co-ordination mode of the CP_3 ligand from η^2 to η^3 can be tested by the inspection of the consequential ^{31}P-{^1H} NMR spectrum. For **2a**, the signal due to the non-co-ordinated phosphorus atom has disappeared and a new AMNX spin system is now observed, with chemical shifts and coupling constants in agreement with the co-ordination of the three phosphorus atoms of the tripod ligand to the metal center in a *fac* disposition. The signals centered at δ 5.24 in the ^1H NMR spectrum and δ 122.7 in the ^{13}C-{^1H} spectrum are assigned to a free ethylene molecule, which confirms the displacement of one ethylene ligand from the co-ordination sphere of the metal. The above discussion proves that the η^3 co-ordination of the CP_3 fragment is as indicated in **III**. Unfortunately, all attempts to isolate *trans*-$[Mo(C_2H_4)(\eta^3\text{-}CP_3)(CO)(PMe_3)]$ have been unsuccessful.

Experimental

Microanalyses were carried out by Pascher Microanalytical Laboratory, Remagen (Germany), and by the Microanalytical Service of the University of Sevilla. Infrared spectra were recorded on Perkin-Elmer models 684 or 883 spectrophotometers. Proton, ^{13}C and ^{31}P NMR spectra were run on Varian XL-200, Bruker AMX-300 and Bruker AMX-500 spectrometers. The ^{31}P shifts were measured with respect to external 85% H_3PO_4; ^{13}C NMR spectra were referenced using the ^{13}C resonance of the solvent as an internal standard but are reported with respect to $SiMe_4$. ^1H NMR spectra were referenced to $SiMe_4$. All preparations and other operations were carried out under oxygen-free nitrogen following conventional Schlenk techniques. Solvents were dried and degassed before use. The light petroleum used had b.p. 40–60 °C.

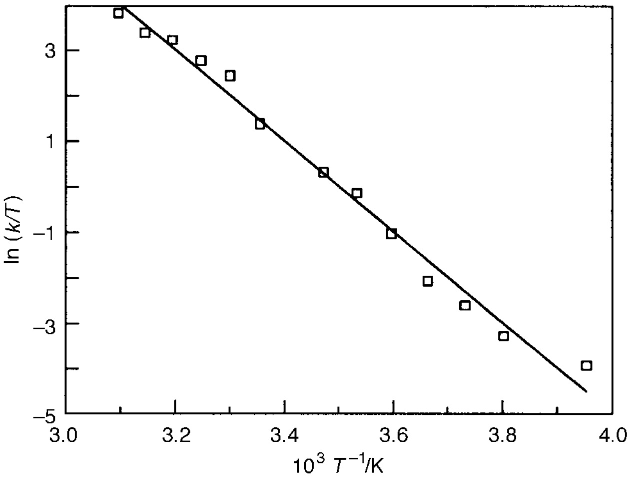
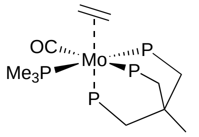


Fig. 4 Eyring plot for $[Mo(C_2H_4)_2(\eta^2\text{-}CP_3)(CO)(PMe_3)]$ **2a**



III

Preparations

***trans*-$[M(C_2H_4)_2(\eta^2\text{-}CP_3)(PMe_3)_2]$ (M = Mo 1a or W 1b).** To a solution of *trans*-$[Mo(C_2H_4)_2(PMe_3)_4]$ (0.49 g, 1.1 mmol) in light petroleum (40 cm^3) was added CP_3 (1.3 cm^3 of a *ca.* 0.9 M solution in toluene) *via* syringe. The resulting mixture was stirred at room temperature for 2 h after which the volatiles were removed under vacuum. Crystallization of the above solid residue from acetone produced complex **1a** as pale yellow crystals (75%) (Found: C, 45.5; H, 9.6. $C_{21}H_{53}MoP_5$ requires C, 45.3; H, 9.5%). ^1H NMR (200 MHz, C_6D_6): δ 1.22 [d, $P(CH_3)(CH_3)$, $^2J(H-P) = 5$], 1.14 (br, CH_2-P non-co-ordinated), 1.10 [d, $P(CH_3)(CH_3)$, $^2J(H-P) = 5$], 0.96 [d, $P(CH_3)_3$, $^2J(H-P) = 4$], 0.92 (s, CH_3-C), 0.86 [d, $P(CH_3)(CH_3)$, $^2J(H-P) = 3.1$], 0.85 [d, $P(CH_3)_2$ non-co-ordinated, $^2J(H-P) = 3.1$] and 0.76 [d, $P(CH_3)(CH_3)$, $^2J(H-P) = 2.8$ Hz], other methylene signals appear as multiplets in the range δ 1.1–1.7 and are partially obscured by the P–Me resonances. ^{31}P-{^1H} NMR (81 MHz, C_6D_6): δ 9.6 [dt, PMe_2, $^2J(P-P)_{cis} = 22.0$, $^2J(P-P)_{trans} = 102.8$], 6.1 [dt, PMe_2, $^2J(P-P)_{cis} = 22.0$, $^2J(P-P)_{trans} = 102.8$], 3.1 [dt, PMe_3, $^2J(P-P)_{cis} = 22.0$, $^2J(P-P)_{trans} = 103.3$], 0.5 [dt, PMe_3, $^2J(P-P)_{cis} = 21.4$, $^2J(P-P)_{trans} = 103.3$ Hz] and −62.5 (s, PMe_2 non-co-ordinated). ^{13}C-{^1H} NMR (75 MHz, C_6D_6): δ 12.9 [d, CH_3-P, $^1J(C-P) = 3.7$], 14.3 [d, CH_3-P, $^1J(C-P) = 6.1$], 16.0 [d, $P(CH_3)(CH_3)$ non-co-ordinated, $^1J(C-P) = 2.7$], 16.2 [d, $P(CH_3)(CH_3)$ non-co-ordinated, $^1J(C-P) = 2.8$], 19.5 [d, $P(CH_3)_3$, $^1J(C-P) = 13.2$], 19.6 [d, $P(CH_3)_3$, $^1J(C-P) = 13.7$], 21.9 [d, CH_3-P, $^1J(C-P) = 21.9$], 23.1 [d, CH_3-P, $^1J(C-P) = 21.7$], 25.6 (two overlapped m, C_2H_4), 26.3 (m, C_2H_4), 26.8 (m, C_2H_4), 28.3 [dt, CH_3-C, $^3J(C-P) = 9.5$, $^3J(C-P) = 3.8$], 38.4 [dt, CH_3-C, $^2J(C-P) = 11.8$, $^2J(C-P) = 3.5$], 45.2 [dd, CH_2–P, ^1J(C–P) = 12.6, ^2J(C–P) = 8.0], 46.7 [dd, CH_2–P, ^1J(C–P) = 14.7, ^2J(C–P) = 7.8] and 54.3 [dt, CH_2–P non-co-ordinated, ^1J(C–P) = 15.9, ^3J(C–P) = 6.9 Hz].

The complex **1b** was obtained following a similar procedure using the compound *trans*-[W$(C_2H_4)_2(PMe_3)_4$] as the starting material (65%) (Found: C, 39.2; H, 8.3. $C_{21}H_{53}P_5W$ requires C, 39.1; H, 8.2%). ^1H NMR (500 MHz, C_6D_6): δ 1.66 [dd, H(3), ^2J(H–H) = 14, ^2J(H–P) = 5], 1.62 [dd, H(1), ^2J(H–H) = 13, ^2J(H–P) = 5], 1.41 [dd, H(1′), ^1J(H–H) = 13, ^2J(H–P) = 10], 1.35 [d, CH_3(8), ^2J(H–P) = 5.5], 1.24 [d, CH_3(6), ^2J(H–P) = 5.5], 1.22 [m, H(3′)], 1.11 [m, CH_2(5)], 1.06 [d, $P(CH_3)_3$, ^2J(H–P) = 5.3], 1.05 [d, $P(CH_3)_3$, ^2J(H–P) = 5.3], 1.02 (m, C_2H_4), 0.93 [s, CH_3(4)], 0.89 [d, CH_3(7), ^2J(H–P) = 5.5], 0.87 [d, P(CH_3)(CH_3) non-co-ordinated, ^2J(H–P) = 3.3], 0.86 [d, P(CH_3)(CH_3) non-co-ordinated, ^2J(H–P) = 3.2 Hz] and 0.80 [m, CH_3(9)], the C_2H_4 signals are partially obscured by the P–Me resonances. ^{31}P-{^1H} NMR (81 MHz, C_6D_6): δ −29.6 [dt, PMe_2, $^2J(P–P)_{cis}$ = 11.3, $^2J(P–P)_{trans}$ = 100.5], −32.5 [dt, PMe_2, $^2J(P–P)_{cis}$ = 12.1, $^2J(P–P)_{trans}$ = 101.8], −35.7 [dt, PMe_3, $^2J(P–P)_{cis}$ = 12.5, $^2J(P–P)_{trans}$ = 99.8], −37.7 [dt, PMe_3, $^2J(P–P)_{cis}$ = 13.0, $^2J(P–P)_{trans}$ = 100.9 Hz] and −64.1 (s, PMe_2 non-co-ordinated). ^{13}C-{^1H} NMR (125 MHz, C_6D_6): δ 10.7 [d, CH_3(7), ^1J(C–P) = 8.5], 12.6 [d, CH_3(9), ^1J(C–P) = 11.3], 16.0 [d, P(CH_3)(CH_3) non-co-ordinated, ^1J(C–P) = 6.1], 16.1 [d, P(CH_3)(CH_3) non-co-ordinated, ^1J(C–P) = 6.3], 16.7 (m, C_2H_4), 16.9 (m, C_2H_4), 17.7 (m, C_2H_4), 18.0 (m, C_2H_4), 19.3 [d, $P(CH_3)_3$, ^1J(C–P) = 12.6], 19.4 [d, $P(CH_3)_3$, ^1J(C–P) = 13.3], 22.1 [d, CH_3(8), ^1J(C–P) = 23.9], 23.7 [d, CH_3(6), ^1J(C–P) = 26.5], 28.4 [dt, CH_3–C, CH_3(4), ^3J(C–P) = 9.5, ^3J(C–P) = 3.8], 39.1 [dt, CH_3–*C*, C(2), ^2J(C–P) = 11.8, ^2J(C–P) = 3.0], 44.0 [dd, CH_2(3), ^1J(C–P) = 18.0, ^2J(C–P) = 8.5], 45.9 [dd, CH_2(1), ^1J(C–P) = 19.9, ^2J(C–P) = 8.0] and 54.9 [dt, CH_2(5), ^1J(C–P) = 15.8, ^3J(C–P) = 8.4 Hz]. The ^1H-{^{31}P} and ^{31}P-{^1H}–^1H NMR spectra have been performed in order to corroborate the proposed assignments.

***trans*-[M$(C_2H_4)_2(\eta^2\text{-}CP_3)$(CO)($PMe_3$)] (M = Mo 2a or W 2b).** A solution of *trans*-[Mo$(C_2H_4)_2(\eta^2\text{-}CP_3)(PMe_3)_2$] (0.18 g, 0.32 mmol) in Et_2O (20 cm^3) was pressurized with CO (2 atm) in a pressure bottle. After 1 h the volatiles were removed under vacuum. The residue was extracted with light petroleum (20 cm^3) and white crystals of **2a** were obtained after cooling at −30 °C overnight (75%) (Found: C, 44.7; H, 9.0. $C_{19}H_{44}MoOP_4$ requires C, 44.9; H, 8.7%). IR: ν(CO) 1840s (br) (Nujol), 1862s (light petroleum) cm^{-1}. ^1H NMR (200 MHz, C_6D_6, 293 K): δ 0.93 [d, $P(CH_3)_3$, ^2J(H–P) = 5.6], 0.81 [d, $P(CH_3)_2$ non-co-ordinated, ^2J(H–P) = 3.3 Hz], 0.79 (s, CH_3–C), other very broad resonances appear in the range δ 0.6–1.6. ^{31}P-{^1H} NMR (125 MHz, [$^2H_8$]toluene, 323 K, AMX spin system): δ 1.6 [dd, P_A, *J*(A–X) = 24, *J*(A–M) = 95], −6.4 [dd, P_M, *J*(M–A) = 95, *J*(M–X) = 27], −14.2 [pseudo t, P_X, *J*(X–A) = *J*(X–M) = 25 Hz] and −69.3 (s, PMe_2 non-co-ordinated). ^{31}P-{^1H} NMR (125 MHz, [$^2H_8$]toluene, 253 K, two AMX spin systems): δ species A, 2.1 [dd, P_A, *J*(A–X) = 25, *J*(A–M) = 94], −5.2 [dd, P_M, *J*(M–A) = 94, *J*(M–X) = 27], −12.7 [pseudo t, P_X, *J*(X–A) = *J*(X–M) = 25] and −70.1 (s, PMe_2 non-co-ordinated); species B, 0.8 [dd, P_A, *J*(A–X) = 26, *J*(A–M) = 92], −5.1 [dd, P_M, *J*(M–A) = 92, *J*(M–X) = 27], −15.6 [pseudo t, P_X, *J*(X–A) = *J*(X–M) = 26 Hz] and −70.4 (s, PMe_2 non-co-ordinated). ^{13}C-{^1H} NMR (125 MHz, [$^2H_8$]toluene, 300 K): δ 226.8 [dt, CO, ^2J(C–P) = 38, ^2J(C–P) = 9], 54.1 (br s, CH_2–P non-co-ordinated), 44.0 (br s, CH_2–P), 43.6 (br s, CH_2–P), 39.4 [dt, CH_3–*C*, ^2J(C–P) = 12, ^2J(C–P) = 3], 29.1 (br, C_2H_4), 17.6 [d, $P(CH_3)_3$, ^1J(C–P) = 17], 16.4 [d, P(CH_3)(CH_3) non-co-ordinated, ^1J(C–P) = 13] and 16.3 [d, P(CH_3)(CH_3) non-co-ordinated, ^1J(C–P) = 13 Hz]. ^{13}C-{^1H} NMR (125 MHz, [$^2H_8$]toluene, 223 K, selected resonances): δ species A, 31.2, 28.6, 13.5 and 11.8 (m, PMe_2 co-ordinated), species B, 29.2, 26.8, 12.1 and 10.7 (m, PMe_2 co-ordinated).

Following a similar procedure compound **2b** was obtained (65%) (Found: C, 38.2; H, 7.6. $C_{19}H_{44}OP_4W$ requires C, 38.2; H, 7.4%). IR (Nujol): ν(CO) 1840s (br) (Nujol), 1864s (light petroleum) cm^{-1}. ^1H NMR (200 MHz, C_6D_6, 293 K): δ 1.03 [d, $P(CH_3)_3$, ^2J(H–P) = 6.2], 0.82 [d, $P(CH_3)_2$ non-co-ordinated, ^2J(H–P) = 3.2 Hz], 0.79 (s, CH_3–C), other very broad resonances appear in the range δ 0.4–1.5. ^{31}P-{^1H} NMR (81 MHz, C_6D_6, 293 K): δ −33.0 (br, species A), −30.6 (br, species B), −28.0 [dd, *J*(P–P) = 88, *J*(P–P) = 21], −22.2 [br d, *J*(P–P) = 88, species A], −21.1 [br d, *J*(P–P) = 88 Hz, species B] and −58.5 (br s). ^{31}P-{^1H} NMR [81 MHz, $(CD_3)_2CO$, 203 K, two AMX spin systems]: δ species A, −19.3 [dd, P_A, *J*(A–X) = 18, *J*(A–M) = 87, ^1J(A–W) = 228], −25.5 [dd, P_M, *J*(M–A) = 87, *J*(M–X) = 18, ^1J(M–W) = 240], −30.1 [pseudo t, P_X, *J*(X–A) = *J*(X–M) = 18, ^1J(X–W) = 176] and −58.3 (s, PMe_2 non-co-ordinated); species B, −21.4 [dd, P_A, *J*(A–X) = 18, *J*(A–M) = 85, ^1J(A–W) = 228], −25.7 [dd, P_M, *J*(M–A) = 85, *J*(M–X) = 20, ^1J(M–W) = 234], −32.6 [dd, P_X, *J*(X–A) = 18, *J*(X–M) = 20, ^1J(X–W) = 172 Hz] and −58.7 (s, PMe_2 non-co-ordinated). ^{13}C-{^1H} NMR (50 MHz, C_6D_6): 217.7 (m, CO), 54.6 (br, CH_2–P non-co-ordinated, species A), 53.0 (br, CH_2–P non-co-ordinated, species B), 42.3 (br, 2 CH_2–P), 39.2 [d, CH_3–C, *J*(C–P) = 13], 27.8 (s, CH_3–*C*), 30–26 [two br m, $P(CH_3)_2$ species A and B], 23–17.5 [several br m, $P(CH_3)_2$ and C_2H_4 species A and B], 16.8 [br d, $P(CH_3)_3$], 16.1 [d, P(CH_3)(CH_3) non-co-ordinated, ^1J(C–P) = 14] and 15.9 [d, P(CH_3)(CH_3) non-co-ordinated, ^1J(C–P) = 15 Hz].

Heating *trans*-[Mo$(C_2H_4)_2(\eta^2\text{-}CP_3)$(CO)($PMe_3$)]. An NMR tube was charged with a solution of the compound *trans*-[Mo$(C_2H_4)_2(\eta^2\text{-}CP_3)$(CO)($PMe_3$)] in C_6D_6 and sealed. After heating at 80 °C for 45 min, the solution changed from yellow to red, and a ^{31}P-{^1H} NMR spectrum was recorded at room temperature. ^{31}P-{^1H} NMR (81 MHz, C_6D_6, AMNX spin system): δ −10.0 [q, ^2J(P–P) = 30], 0.4 [ddd, ^2J(P–P) = 75, ^2J(P–P) = 30, ^2J(P–P) = 25], 2.7 [td, ^2J(P–P) = 30, ^2J(P–P) = 25] and 6.4 [dt, ^2J(P–P) = 75, ^2J(P–P) = 30 Hz].

***trans*-[Mo$(C_2H_4)_2(\eta^2\text{-}CP_3)$($CNBu^t$)($PMe_3$)] 3.** A solution of **1a** (0.21 g, 0.37 mmol) in light petroleum (40 cm^3) was mixed with 1.1 equivalents of $CNBu^t$ (0.41 cm^3 of a 1 M solution in tetrahydrofuran) and the mixture was stirred for 1 h. The solvent was then removed under vacuum and the residue extracted with light petroleum (10 cm^3). Filtration and crystallization of the resulting solution at −78 °C afforded **3** as yellow crystals (65%). IR (Nujol): ν(CN) 1970s (br) cm^{-1}. ^1H NMR (200 MHz, C_6D_6, 293 K): 1.14 (s, Bu^t), 1.04 [d, $P(CH_3)_3$, ^2J(H–P) = 5], 0.92 (s, CH_3–C) and 0.84 [d, $P(CH_3)_2$ non-co-ordinated, *J*(H–P) = 3.5 Hz]. ^{31}P-{^1H} NMR (81 MHz, C_6D_6, 293 K): δ 9.8 [br d, *J*(P–P) = 100, species A], 8.7 [br d, *J*(P–P) = 100, species B], 2.0 [dd, *J*(P–P) = 100, *J*(P–P) = 25 Hz], 0.6 (br, species A), −1.4 (br, species B) and −63.5 (br s). ^{31}P-{^1H} NMR [81 MHz, $(CD_3)_2CO$, 223 K, two AMX spin systems]: δ species A, 14.7 [dd, P_A, *J*(A–X) = 22, *J*(A–M) = 101], 7.9 [dd, P_M, *J*(M–A) = 101, *J*(M–X) = 22], 4.0 [pseudo t, P_X, *J*(X–A) = *J*(X–M) = 22 Hz] and −58.1 (s, PMe_2 non-co-ordinated); species B, 13.3 [dd, P_A, *J*(A–X) = 22, *J*(A–M) = 99], 7.8 [dd, P_M, *J*(M–A) = 99, *J*(M–X) = 22], 5.8 [pseudo t, P_X, *J*(X–A) = *J*(X–M) = 22 Hz] and −58.8 (s, PMe_2 non-co-ordinated).

Line shape analysis of 2a

The ^{31}P-{^1H} NMR (125 MHz) spectra used for this study have been recorded over the temperature range 323–253 K in [$^2H_8$]-toluene. The chemical shifts and coupling constants at the low-temperature limiting spectrum were used as inputs to the DNMR3[28] simulation program. The simulated spectra obtained were compared with the experimental ones (see Fig. 3) and the great similarities confirm the proposed ethylene-rotamer interconversion through a concerted conrotatory mechanism. An Eyring plot (Fig. 4) gave a straight line

($R = 0.994$) and the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ approximate activation parameters were obtained from the slope and intercept, 83 kJ mol^{-1} and 93 J mol^{-1} K^{-1}, respectively. Application of the Eyring equation gave an approximate $\Delta G^{\ddagger}$ value of 55 kJ mol^{-1} at 298 K. The use of the exchange rate constants in the Arrhenius equation gave the energy of activation: $E_a = 85.5$ kJ mol^{-1}.

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References

1 H. A. Mayer and W. C. Kaska, *Chem. Rev.*, 1994, **94**, 1239 and refs. therein; F. A. Cotton and B. Hong, *Prog. Inorg. Chem.*, 1992, **40**, 179 and refs. therein; C. Bianchini, A. Meli, M. Peruzzini, F. Vizza and F. Zanobini, *Coord. Chem. Rev.*, 1992, **120**, 193; C. Mealli, C. A. Ghilardi and A. Orlandini, *Coord. Chem. Rev.*, 1992, **120**, 361.

2 *Homogeneous Catalysis with Metal-Phosphine Complexes,* ed. L. H. Pignolet, Plenum Press, New York, 1983; *Catalytic Asymmetric Synthesis*, ed. I. Ojima, VCH, Weinheim, 1993; H. Brunner and W. Zettlmeier, *Handbook of Enantioselective Catalysis,* VCH, Weinheim, 1993.

3 E. Carmona, J. M. Marín, M. L. Poveda, J. L. Atwood and R. D. Rogers, *J. Am. Chem. Soc.*, 1983, **105**, 3014; E. Carmona, A. Galindo, M. L. Poveda and R. D. Rogers, *Inorg. Chem.*, 1985, **24**, 4033.

4 R. Alvarez, E. Carmona, A. Galindo, E. Gutiérrez, J. M. Marín, A. Monge, M. L. Poveda, C. Ruiz and J. M. Savariault, *Organometallics*, 1989, **8**, 2430.

5 E. Carmona, A. Galindo, A. Monge, M. A. Muñoz, M. L. Poveda and C. Ruiz, *Inorg. Chem.*, 1990, **29**, 5074.

6 A. Galindo, A. Pastor, P. Pérez and E. Carmona, *Organometallics*, 1993, **12**, 4443.

7 C. Collazo, M. M. Conejo, A. Pastor and A. Galindo, *Inorg. Chim. Acta*, 1997, in the press.

8 T. Suzuki, K. Isobe, K. Kashiwabara, J. Fujita and S. Kaizaki, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 3779 and refs. therein; E. G. Thaler, K. Folting, J. C. Huffman and K. G. Caulton, *J. Organomet. Chem.*, 1989, **376**, 343.

9 F.-W. Grevels, J. Jacke, P. Betz, C. Krüger and Y.-H. Tsay, *Organometallics*, 1989, **8**, 293; F.-W. Grevels, J. Jacke and S. Özkar, *J. Am. Chem. Soc.*, 1987, **109**, 7536; B. H. Weiller and E. R. Grant, *J. Am. Chem. Soc.*, 1987, **109**, 1252; M. F. Gregory, S. A. Jackson, M. Poliakoff and J. J. Turner, *J. Chem. Soc.*, *Chem. Commun.*, 1986, 1175.

10 A. M. Arif, J. G. Hefner, R. A. Jones and B. R. Whittlesey, *Inorg. Chem.*, 1986, **25**, 1080.

11 (*a*) P. K. Baker, S. J. Coles, M. B. Hursthouse, M. M. Meehan and S. D. Ridyard, *J. Organomet. Chem.*, 1995, **503**, C8; (*b*) A. Muth, G. Reinhard, G. Huttner, T. Seitz, T. Klein and L. Zsolnai, *Z. Naturforsch.*, *Teil B*, 1994, **49**, 889; (*c*) A. J. Blake, R. O. Gould, M. A. Halcrow and M. Schröder, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 2909; (*d*) G. V. Goeden, J. C. Huffman and K. G. Caulton, *Inorg. Chem.*, 1986, **25**, 2484; (*e*) A. L. Balch, R. R. Guimerans and J. Linehan, *Inorg. Chem.*, 1985, **24**, 290; (*f*) M. Di Vaira, S. Midollini and L. Sacconi, *Inorg. Chem.*, 1981, **20**, 3430; (*g*) M. R. Churchill, A. L. Rheingold and R. L. Keiter, *Inorg. Chem.*, 1981, **20**, 2730; (*h*) C. Bianchini, P. Dapporto and A. Meli, *J. Organomet. Chem.*, 1979, **174**, 205; (*i*) W. O. Siegl, S. J. Lapporte and J. P. Collman, *Inorg. Chem.*, 1973, **12**, 674.

12 A. Galindo, *J. Chem. Educ.*, 1993, **70**, 325.

13 A. G. Orpen, *Chem. Soc. Rev.*, 1993, 191; D. A. V. Morton and A. G. Orpen, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 641.

14 S. Beyreuther, J. Hunger, G. Huttner, S. Mann and L. Zsolnai, *Chem. Ber.*, 1996, **129**, 745.

15 K. M. Norenberg, C. M. Shoemaker and M. Zimmer, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 1521; M. F. DaCruz and M. Zimmer, *Inorg. Chem.*, 1996, **35**, 2872 and refs. therein; J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, 1972, **11**, 156.

16 E. Farkas, L. Kollár, M. Moret and A. Sironi, *Organometallics*, 1996, **15**, 1345.

17 R. R. Guimerans, M. M. Olmstead and A. L. Balch, *J. Am. Chem. Soc.*, 1983, **105**, 1677; *Inorg. Chim. Acta*, 1983, **75**, 199.

18 T.-Y. Hsieh, M.-C Cheng, S.-M. Peng and S.-T. Liu, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 3499; S.-T. Liu, H.-E. Wang, L.-M. Yiin, S.-C. Tsai, K.-J. Liu, Y.-M. Wang, M.-C. Cheng and S.-M. Peng, *Organometallics*, 1993, **12**, 2277; H.-E. Wang, M.-C. Cheng, G.-H. Lee, S.-M. Peng and S.-T. Liu, *J. Organomet. Chem.*, 1993, **445**, 171; S.-T. Liu, G.-J. Liu, C.-H. Yieh, M.-C. Cheng and S.-M. Peng, *J. Organomet. Chem.*, 1990, **387**, 83; S.-T. Liu, H.-E. Wang, M.-C. Cheng and S.-M. Peng, *J. Organomet. Chem.*, 1989, **376**, 333.

19 C. Bachmann, J. Demuvynck and A. J. Veillard, *J. Am. Chem. Soc.*, 1978, **100**, 2366.

20 C. S. Kraihanzel, J. M. Ressner and G. M. Gray, *Inorg. Chem.*, 1982, **21**, 879.

21 E. Carmona, A. Galindo, J. M. Marín, E. Gutiérrez, A. Monge and C. Ruiz, *Polyhedron*, 1988, **7**, 1831.

22 C.-H. Lai and C.-H. Cheng, *Organometallics*, 1993, **12**, 3561; C.-H. Lai, C.-H. Cheng, W.-C. Chou and S.-L. Wang, *Organometallics*, 1993, **12**, 1105, 3418; C.-H. Lai, C.-H. Cheng, C.-Y. Cheng and S.-L. Wang, *J. Organomet. Chem.*, 1993, **458**, 147; C.-H. Lai, C.-H. Cheng, F.-L. Liao and S.-L. Wang, *Inorg. Chem.*, 1993, **32**, 5658.

23 E. Carmona, A. K. Hughes, M. A. Muñoz, D. M. O'Hare, P. J. Pérez and M. L. Poveda, *J. Am. Chem. Soc.*, 1991, **113**, 9210.

24 J. Sandström, *Dynamic NMR Spectroscopy*, Academic Press, New York, 1982, pp. 93–97.

25 J. W. Byrne, H. V. Blaser and J. A. Osborn, *J. Am. Chem. Soc.*, 1975, **97**, 3871.

26 F.-W. Grevels, M. Lindemann, R. Benn, R. Goddard and C. Krüger, *Z. Naturforsch.*, *Teil B*, 1980, **35**, 1298.

27 M. Jaroszewski, T. Szymanska-Buzar, M. Wilgocki and J. J. Ziólkowski, *J. Organomet. Chem.*, 1996, **509**, 19.

28 DNMR Quantum Chemical Program Exchange, Indiana University QCPE Program No. 466.

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