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Some P–H bond substitution derivatives and fluxionality of $\text{Cp}_2\text{Mo}_2(\mu\text{-H})(\mu\text{-PPh})(\text{CO})_4$

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Abstract

Reaction of PH_2Ph with $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ ($\text{Mo}\equiv\text{Mo}$) results in sequential formation of $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PH}_2\text{Ph})_2$ and fluxional $\text{Cp}_2\text{Mo}_2(\mu\text{-H})(\mu\text{-PPh})(\text{CO})_4$. Proton abstraction from $\text{Cp}_2\text{Mo}_2(\mu\text{-H})(\mu\text{-PPh})(\text{CO})_4$ affords $[\text{Cp}_2\text{Mo}_2(\mu\text{-PPh})(\text{CO})_4]^-$ while reaction with $[\text{Ph}_3\text{C}][\text{PF}_6]$ yields fluxional $\text{Cp}_2\text{Mo}_2(\mu\text{-H})(\mu\text{-PPh})(\text{CO})_4$.

Introduction

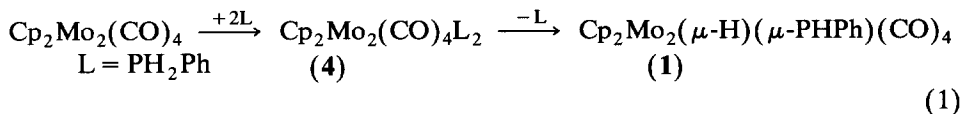
The use of clusters supported on refractory oxides for the purpose of preparing specific surface ensembles for catalysis continues to attract attention [1–3]. Use of heteroatom clusters has been suggested as a means of inhibiting cluster fragmentation via reactions with the surface [4,5]. We have reported the preparation of several sulfido bimetallic clusters [6] and their use as supported catalyst precursors and models [7,8]. We sought to prepare an analogous series of phosphinidene clusters [8] using $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu\text{-PPh})(\mu\text{-H})$ (**1**) as a cluster synthon. Although **1** proved to be a poor synthon for clusters containing the Mo_2PPh group, we found several aspects of the fluxional behavior and reactivity of **1** that merited reporting.

Results and discussion

Complex **1** has been prepared previously by the reaction of PhPH_2 with $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ (**2**) at 90°C in toluene [9]. Since **2** is converted to $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{Mo}\equiv\text{Mo})$ (**3**) under these conditions [10], we allowed PhPH_2 to react directly with

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3 at room temperature. Under these conditions, the intermediate bis(phosphine) adduct **4** (eq. 1) precipitates from solution and may be recovered in 69% yield.



In the IR spectrum of **4**, the $\nu(\text{CO})$ bands appear at the relatively low frequencies of 1862sh and 1844 cm^{-1} . Such low frequencies suggest that the steric bulk of the two phosphine ligands forces the carbonyl groups into semi-bridging positions. The appearance of one peak each for the Cp and PH_2 protons in the ^1H NMR spectrum and only one signal for the carbonyl carbons in the ^{13}C NMR indicates that **4** is fluxional at room temperature and has apparent C_{2v} symmetry on the NMR time scale. The low solubility and consequent poor signal to noise ratio made a detailed line shape analysis impractical.

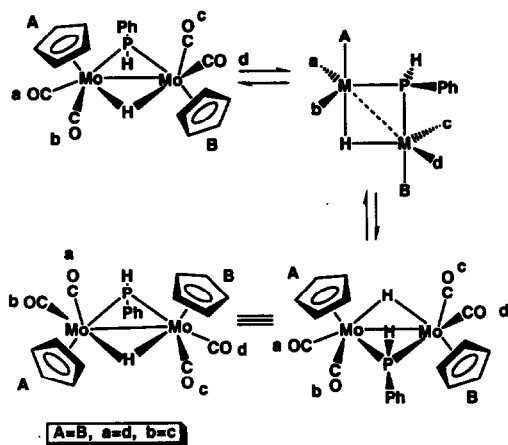
The reaction of triply bonded **3** with PhPH_2 is similar to the reactions of **3** with PPh_3 [10] and with PH_3 or MePH_2 [11]. In the former reaction, the bis(phosphine) adduct is isolated, but with the latter phosphines, the bis(adducts) were detected as intermediates in the formation of μ -phosphide complexes.

Prolonged stirring of toluene suspensions of **4** resulted in the expected hydride **1**. This reaction was conveniently followed by ^1H NMR spectroscopy. Freshly prepared CDCl_3 samples of **4** showed a single, phosphorus-coupled Cp resonance [δ 4.83 (d, 10H, $J(\text{PH}) = 2$ Hz)] together with signals attributable to the PH_2Ph ligands. In particular, a large $J(\text{PH})$ coupling constant of 347 Hz was seen for the phosphorus bound hydrogens. After 4 h, a low frequency signal [δ -12.04 (d, 1H, $J(\text{PH}) = 37.5$ Hz)] associated with the hydride of **1** grew in. Other signals due to the Cp and phosphide ligand of **1** also appeared at the same rate while those due to **4** disappeared. Despite the formation of other minor products, orange **1** was easily isolated upon completion of the reaction.

As reported previously [9], the ^1H NMR spectra of complex **1** are temperature dependent. At low temperatures (below -20°C) two sharp cyclopentadienyl signals are seen, consistent with a transoid geometry isostructural with that of $\text{Cp}_2\text{Mo}_2(\mu\text{-H})(\mu\text{-PMe}_2)(\text{CO})_4$ [12]. On warming, the Cp peaks gradually coalesce indicating site exchange. An activation energy ΔG^\ddagger (21°C) of 62.2 ± 0.6 kJ mol^{-1} can be calculated for this process [13].

The ^{13}C NMR spectrum of **1** in $\text{C}_6\text{D}_5\text{CD}_3$ is also temperature dependent. Again the coalescence of the two Cp resonances was seen. More interestingly, the four carbonyl resonances that are observed at -40°C [δ 235.6 (CO); 236.8 (CO); 241.6 (d, $J(\text{PC}) = 20.5$ Hz, CO); 242.7 (d, $J(\text{PC}) = 24$ Hz, CO)] collapse to a single broad signal [δ 238.2 (CO)] at 50°C . Further heating of the sample was not possible due to decomposition. The value of ΔG^\ddagger estimated either from the width of the Cp resonance after coalescence or from coalescence temperature (50°C) of the CO signals is 60 ± 2 kJ mol^{-1} . Since this value is the same within experimental error as determined from the proton spectra, we conclude that the same processes are involved in averaging the CO or Cp environments.

Without the benefit of the high temperature ^{13}C NMR results, previous workers ascribed the fluxional process to isomerizations occurring via the trigonal bipyramidal (TBP) intermediates shown in Scheme 1 [9]. In the high temperature limit, this



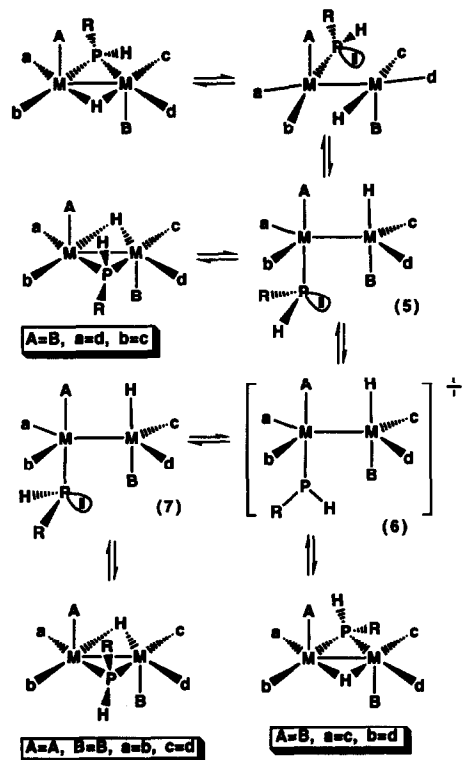
Scheme 1.

isomerization averages the environments of the CO groups into pairs ($a \leftrightarrow d$, $c \leftrightarrow b$) as well as making the Cp groups equivalent.

In a classic study of the fluxional behavior of $\text{CpMo}(\text{CO})_2\text{XR}$ complexes (X = phosphine or phosphite, R = H or alkyl), Faller and Anderson showed that these complexes undergo degenerate *cis* \leftrightarrow *cis* isomerizations as well as *cis* \leftrightarrow *trans* isomerizations [14]. They further showed that these isomerizations most likely occur via TBP intermediates, and that such intermediates with CO in an axial position (*i.e.* *trans* to the Cp group) are some 13–17 kJ mol^{-1} higher in energy than those with X or R groups in the axial position. Rearrangement pathways leading to the *trans* isomers also had higher activation energies than the *cis* \leftrightarrow *cis* pathways. The interconversions shown in Scheme 1 are thus consistent with Faller and Anderson's results, but are insufficient to account for the observed high temperature limiting spectra.

The symmetry elements in the time averaged structure consist of a C_2 axis passing through the bridging atoms, P and H, and a mirror plane perpendicular to this axis and containing the Mo–Mo bond. Therefore, the μ -P and μ -H must interchange places and the RPH group must also “rotate” such that R and H become averaged. These averaging motions require that the P atom undergo inversion of configuration (*e.g.* $5 \rightarrow 6 \rightarrow 7$ in Scheme 2) if high energy intermediates with carbonyl groups in the axial positions are avoided. Since the observed activation energies are similar to those measured by Faller for *cis* \leftrightarrow *cis* isomerizations, we conclude that axial P or H atoms are present in the intermediates as shown in Scheme 2. Although there exist many possible variations of the details, the fluxional process must entail the essential features shown in the scheme.

Compound 1 showed little reactivity towards traditional cluster synthons such as $\text{Co}_2(\text{CO})_8$ or Cp_2Ni . However, the hydride in 1 is markedly acidic. In the presence of D_2O and NEt_3 in CDCl_3 , extensive deuterium for hydrogen exchange was noticeable after 1 h by ^1H NMR spectroscopy. In fact, 1 was readily deprotonated with $^n\text{BuLi}$ in THF (tetrahydrofuran) at -80°C to form the purple anion $[\text{Cp}_2\text{Mo}_2(\mu\text{-PPh})(\text{CO})_4]^-$ (8). Solutions of 8 are exceedingly air and moisture sensitive. For example, the IR spectrum of 8 in dry, anerobic cells showed only two



Scheme 2.

bands [$\nu(\text{CO})$ (THF): 1807s, 1717s cm^{-1}], while the presence of even traces of air leads to the observation of multiple peaks [$\nu(\text{CO})$ (THF): 1882m, 1841s, 1797s, 1775m cm^{-1}]. The ^1H NMR spectrum of the THF reaction mixture showed a single peak each for the Cp [δ 4.72 (s, 5H)] and P-H protons (δ 6.12) suggesting that only one product was formed and that the bridging hydride is removed by base. Collaborative evidence for the formation of **8** was available *via* protonation of solutions of the anion with acetic acid; the hydride **1** was recovered in very high yield (89%). Reaction of **8** with $\text{CD}_3\text{CO}_2\text{D}$ resulted in 60% deuterium incorporation into the hydride. The ^2H NMR of 1- D_1 in CHCl_3 showed a single phosphorus-coupled, low frequency signal [δ -11.88 (d, $J(\text{PD}) = 49.5$, $\mu\text{-D}$)] assigned to the bridging deuteride. Reaction of the anion **8** with transition metal halides, Ph_2ICl or MeI led only to low yields of **1** or (for MeI) $\text{CpMoMe}(\text{CO})_3$.

The complex **1** reacted with $[\text{Ph}_3\text{C}][\text{PF}_6^-]$ in CH_2Cl_2 to give a new species by IR spectroscopy [$\nu(\text{CO})$ (CH_2Cl_2): 1947s, 1887s cm^{-1}] along with some decomposition. Extensive recrystallization allowed the isolation of the new species $\text{Cp}_2\text{Mo}_2(\mu\text{-H})(\mu\text{-PFPh})(\text{CO})_4$ (**9**). Presumably, the fluoride in **9** originated from the PF_6^- counter anion. Certainly *in situ* generation of PF_5 would account for the decomposition observed in the reaction mixture. The hydride in **9** resonates at δ -10.95, a frequency about 1 ppm higher than that for **1**, as a consequence of the presence of the inductively electron withdrawing fluorophosphide. Compound **9** is fluxional. The mechanism of fluxionality is probably identical to that of **1**. A line

shape analysis gave an activation barrier of ΔG^\ddagger (21°C) = 59.2 ± 0.6 kJ mol⁻¹, comparable to that for 1.

Experimental section

General data

Infrared spectra were recorded on a Nicolet 5DX spectrometer. Proton (300.1 MHz) and ¹³C (75.5 MHz) NMR spectra were recorded on a Bruker AM-300 instrument. Deuterium (55.3 MHz) NMR spectra were obtained on a Bruker WM-360. Probe head temperatures were measured before and after the data acquisition with a copper-constantan thermocouple. All coupling constants are in Hertz. Mass spectra were recorded on VG-70-250-S mass spectrometer using either EI or FAB ionization modes. Elemental analyses were performed by the University of Michigan microanalytical service. All operations were performed under a nitrogen atmosphere using rigorously dried and deoxygenated solvents with standard Schlenk techniques. The compound Cp₂Mo₂(CO)₆ was prepared by known procedures [15]. Phenylphosphine, ⁿBuLi, and [Ph₃C][PF₆] (Aldrich) were used as supplied.

Preparation of Cp₂Mo₂(CO)₄(PH₂Ph)₂ (4)

The dimer Cp₂Mo₂(CO)₆ (4.00 g, 8.16 mmol) was suspended in toluene (150 mL) and the suspension refluxed (16 h) with a slow nitrogen purge. The resulting solution of Cp₂Mo₂(CO)₄ (Mo≡Mo) was allowed to cool to ambient temperature and filtered to remove insoluble material. Neat PH₂Ph (1.85 mL, 1.85 g, 16.81 mmol) was added and the mixture stirred (15 min). The red Cp₂Mo₂(CO)₄(PH₂Ph)₂ (4) was collected by filtration and washed with hexane (3 × 15 mL). Concentration of the mother liquors to ca. 50 mL afforded a second crop. Total yield of red Cp₂Mo₂(CO)₄(PH₂Ph)₂ was 3.68 g (69%). Anal. Found: C, 47.82; H, 3.68. C₂₆H₂₄Mo₂O₄P₂ calc.: C, 47.72; H, 3.70%. IR (CH₂Cl₂): ν(CO) 1862sh, 1844s cm⁻¹. ¹H NMR (CDCl₃, 20°C): δ 4.83 (d, 10H, *J*(PH) = 2, Cp); 6.31 (d, 4H, *J*(PH) = 347, PH₂); 7.39–7.51 (m, 6H, Ph-*m* + *p*); 7.60–7.72 (m, 4H, Ph-*o*). ¹³C NMR (CDCl₃, -40°C): δ 90.7 (Cp), 128.7 (d, *J*(PC) = 10, Ph-*m*); 130.0 (Ph-*p*); 132.0 (d, *J*(PC) 10, Ph-*o*); 232.6 (d, *J*(PC) = 26, CO). Due to an inadequate signal-to-noise ratio the Ph-*i* signal was not detected. Poorly soluble 4 does not form concentrated solutions. Mass spectrum (EI): *m/z* 544 [(*M* - PH₂Ph)]⁺.

Preparation of Cp₂Mo₂(μ-H)(μ-PHPh)(CO)₄ (1)

A suspension of Cp₂Mo₂(CO)₄(PH₂Ph)₂ (4) (1.30 g, 1.99 mmol) in toluene (100 mL) was stirred (16 h) at room temperature after which time an orange solution had formed. The solvent was removed and the residue extracted with CH₂Cl₂ (3 × 50 mL). The extracts were filtered through an Al₂O₃ plug and the solvent removed. The orange residue was recrystallized from CH₂Cl₂/hexane to yield orange crystals of Cp₂Mo₂(μ-H)(μ-PHPh)(CO)₄ (1) (0.71 g, 65%). This reaction was not reversible; no reaction of 1 with excess PH₂Ph was observed.

Alternatively, the adduct 4 may be prepared *in situ* by adding 2 equiv. of PhPH₂ to Cp₂Mo₂(CO)₄ [16] in toluene and stirring or refluxing the resultant suspension of 4. Anal.: Found: C, 43.99; H, 3.15. C₂₀H₁₇Mo₂O₄P calc.: C, 44.14; H, 3.15%. IR (CH₂Cl₂): ν(CO) 1940s, 1871s cm⁻¹. ¹H NMR (CDCl₃, -40°C): δ -12.04 (d, 1H,

$J(\text{PH}) = 37.5$, $\mu\text{-H}$); 5.03 (s, 5H, Cp); 5.18 (s, 5H, Cp); 6.53 (d, 1H, $J(\text{PH}) = 354$, PH); 7.24–7.39 (m, 5H, Ph). ^{13}C NMR (CDCl_3 , -40°C): δ 90.38 (Cp); 91.52 (Cp); 128.0 (d, $J(\text{PC}) = 10.5$, Ph-*m*); 128.9 (Ph-*p*); 139.7 (d, $J(\text{PC}) = 10$, Ph-*o*); 139.7 (d, $J(\text{PC}) = 38$, Ph-*i*); 234.6 (CO); 236.1 (CO); 242.0 (d, $J(\text{PC}) = 21$, CO); 242.9 (d, $J(\text{PC}) = 24$, CO). Mass spectrum (EI): m/z 544 [M] $^+$.

Preparation of $[\text{Cp}_2\text{Mo}_2(\mu\text{-PPh})(\text{CO})_4]^-$ (**8**)

$^n\text{BuLi}$ (0.1 mL of 1.76 M hexane solution, standardized by titration, 0.18 mmol) was added to a solution of **1** (0.10 g, 0.18 mmol) in THF at -80°C . The mixture was allowed to come to room temperature (1 h) during which time it became purple. Such solutions were generally used without further purification. When Et_2O containing 12-crown-4 was used as solvent, somewhat impure $[\text{Li}(12\text{-crown-4})][\text{Cp}_2\text{Mo}_2(\mu\text{-PhPh})(\text{CO})_4]$, (Li(12-crown-4)**8**) precipitated in quantitative yield upon addition of the $^n\text{BuLi}$. IR (THF): $\nu(\text{CO})$ 1807s, 1717s cm^{-1} . ^1H NMR (**8**, THF, 20°C): δ 4.72 (s, 5H, Cp). ^1H NMR [Li(12-crown-4)**8**, CD_3CN , 20°C]: δ 3.64 (s, 16H, 12-crown-4); 4.83 (s, 5H, Cp); 6.12 (d, 1H, $J(\text{PH}) = 272$, PH); 7.13–7.23 (m, 3H, Ph-*m* + *p*); 7.30–7.37 (m, 2H, Ph-*o*).

Reaction of $[\text{Cp}_2\text{Mo}_2(\mu\text{-PPh})(\text{CO})_4]^-$ (**8**) with MeCO_2H

A solution of the anion **8** (0.18 mmol) was prepared as above and cooled to -80°C . One drop of MeCO_2H was added and the reaction allowed to come to room temperature (1.5 h) during which time it became orange. The solvent was removed and the residue recrystallized from CH_2Cl_2 /hexane to yield $\text{Cp}_2\text{Mo}_2(\mu\text{-H})(\mu\text{-PPh})(\text{CO})_4$ (**1**) as orange crystals, 89 mg (89%). Similar reaction of **8** with $\text{CD}_3\text{CO}_2\text{D}$ gave an equally high yield of a mixture of **1** and **1-D**₁ in a 40:60 ratio.

Preparation of $\text{Cp}_2\text{Mo}_2(\mu\text{-H})(\mu\text{-PPh})(\text{CO})_4$ (**9**)

Solid $[\text{Ph}_3\text{C}][\text{PF}_6]$ (0.14 g, 0.36 mmol) was added to a solution of **1** (0.20 g, 0.36 mmol) in CH_2Cl_2 (25 mL) at room temperature. The reaction mixture darkened and the IR spectrum [CH_2Cl_2 : $\nu(\text{CO})$ 1947s, 1887s cm^{-1}] indicated the formation of a new species. The mixture was filtered through Celite and the solvent removed. Repeated recrystallization from CH_2Cl_2 /hexane afforded a small amount of orange crystalline **9**, 22 mg, 11%. Anal. Found: C, 42.86; H, 2.82. $\text{C}_{20}\text{H}_{16}\text{FMo}_2\text{O}_4\text{P}$ calc.: C, 42.72; H, 2.87%. IR (CH_2Cl_2): $\nu(\text{CO})$ 1947s, 1887s cm^{-1} . ^1H NMR (CDCl_3 , -40°C): δ -10.95 (d, 1H, $J(\text{PH}) = 41$, *m*-H); 5.01 (s, 5H, Cp); 5.32 (s, 5H, Cp); 7.19–7.49 (m, 5H, Ph). Mass spectrum (EI): m/z 562 [M] $^+$.

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