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Preliminary communication

Synthesis and reactivity of aminomethyldiphenylphosphine complexes of molybdenum. Crystal structure of *cis*-[Mo(CO)₄(Ph₂PCH₂NHC₆H₄Me-*p*)₂]

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Abstract

The phosphines Ph₂PCH₂NHR (R = Bu^t, C₆H₄Me-4) react with [Mo(CO)₄(norbornadiene)] or [Mo(CO)₄(piperidine)₂] to form *cis*-[Mo(CO)₄(Ph₂PCH₂NHR)₂]. The crystal structure has been determined for R = C₆H₄Me-4. Reaction of these complexes with aqueous formaldehyde gives the complexes [Mo(CO)₄{(Ph₂PCH₂)₂-NR}] which were also prepared independently from (Ph₂PCH₂)₂NR.

Simple phosphines PR₃ (R = alkyl, aryl) are extremely important ligands in organometallic chemistry. In recent years functionalised phosphines containing one or more functional groups of various types have been synthesised and their properties investigated [1]. We have been examining the chemistry of phosphines of the type Ph₂PCH₂XH (X = O, NR) containing an active hydrogen, with the aim of using this functionality to construct homo- and hetero-bimetallic complexes. We report here the preparation and some reactivity of the complexes *cis*-[Mo(CO)₄(Ph₂PCH₂NHR)₂] (R = Bu^t, C₆H₄Me-4).

Reaction of [Mo(CO)₄(piperidine)₂] or [Mo(CO)₄(norbornadiene)] with two equivalents of the phosphines Ph₂PCH₂NHR in refluxing dichloromethane gives the complexes *cis*-[Mo(CO)₄(Ph₂PCH₂NHR)₂] (**1a**, R = Bu^t; **1b**, R = C₆H₄Me-4). The phosphines are in a mutually *cis* configuration, as evidenced by their carbonyl IR spectra, which show three absorptions and the ¹³C NMR spectra which exhibit two inequivalent CO environments [2*]. An X-ray diffraction study of **1b** was carried out to see whether there were any special features such as hydrogen bonding, and the molecular structure is shown in Fig. 1. The MoP₂ unit has the expected dimensions with an average Mo–P bond distance of 2.557(3) Å and a P–Mo–P angle of 94.2(1)°, compared with the corresponding 2.555(10) Å and 92.52(5)° for

* This and other references marked with asterisks indicate notes occurring in the list of references.

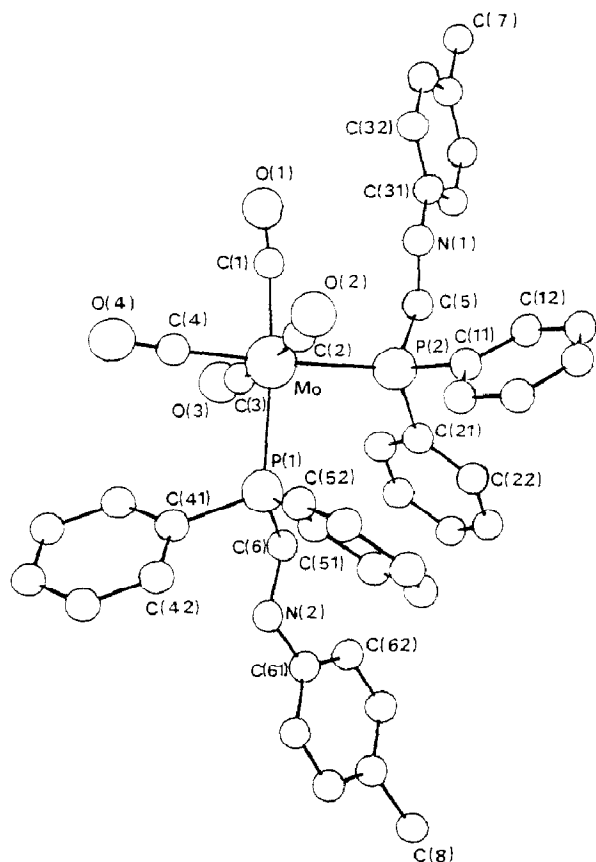
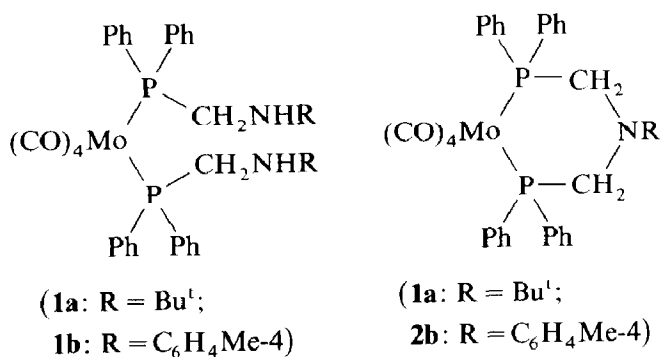


Fig. 1. Molecular structure of *cis* [Mo(CO)₄(Ph₂PCH₂NHR)₂] (**1b**; R = C₆H₄Me-4). Selected bond distances (Å) and bond angles (°). Mo–P(1) 2.553(2), Mo–P(2) 2.560(3), Mo–C(1) 1.995(11), Mo–C(2) 2.025(11), Mo–C(3) 2.000(12), Mo–C(4) 1.976(14), P(2)–Mo–P(1) 94.2(1).

cis-[Mo(CO)₄(PMePh₂)₂] [3]. The average Mo–C distance for CO groups *trans* to the phosphines is 1.986(14) Å, whereas for those *cis* to the phosphines it is 2.013(12) Å; the difference is not statistically significant but the trend is the same as that observed for *cis*-[Mo(CO)₄(PMePh₂)₂] [3].



When complex **1a** was treated in toluene at 100 °C, some *cis*–*trans* isomerisation occurred, two signals being observed in the ³¹P NMR spectrum, one at δ 28.0 (*cis*) and the other at δ 41.3 (*trans*). After 30 min the ratio of *cis* and *trans* isomers was

approximately 2/1. Further heating gave another species (**2a**) (δ 18.8), which was separated by chromatography. The IR spectrum of this complex is very similar to that of **1a**, and the ^1H NMR spectrum and elemental analysis suggested the formulation $[\text{Mo}(\text{CO})_4\{(\text{Ph}_2\text{PCH}_2)_2\text{NBu}^t\}]$. To check this formulation we decided to prepare the complex via another route and reaction of the bisphosphines $(\text{Ph}_2\text{PCH}_2)_2\text{NR}$ ($\text{R} = \text{Bu}^t$, $\text{C}_6\text{H}_4\text{Me-4}$) with $[\text{Mo}(\text{CO})_4(\text{piperidine})_2]$ or $[\text{Mo}(\text{CO})_4(\text{norbornadiene})]$ was found to give complexes **2a** ($\text{R} = \text{Bu}^t$) and **2b** ($\text{R} = \text{C}_6\text{H}_4\text{Me-4}$), respectively, in high yields [4*].

Whilst exploring methods of synthesis [5,6] of the bisphosphines $(\text{Ph}_2\text{PCH}_2)_2\text{NR}$ ($\text{R} = \text{Bu}^t$) we noticed that $\text{Ph}_2\text{PCH}_2\text{NHBu}^t$ reacts with aqueous formaldehyde during 4 h at room temperature to form $(\text{Ph}_2\text{PCH}_2)_2\text{NBu}^t$. Refluxing complexes **1** in toluene with aqueous formaldehyde gives complexes **2** in quantitative yield (by ^{31}P NMR) after ca. 30 h. Thus the coordinated phosphine seems to be much less reactive towards electrophilic attack than the free phosphine, this contrasts with the increased reactivity towards nucleophilic attack found upon coordination of $(\text{Ph}_2\text{P})_2\text{C}=\text{CH}_2$ to a $\text{Mo}(\text{CO})_4$ moiety [7].

Further studies are in progress to investigate the effect of coordination on the reactivity of the phosphines, and also the use of complexes **1** as precursors to heterobimetallic species.

Crystal structure determination

Crystals of complex **1b** were obtained from dichloromethane/petroleum ether. The crystal ($0.31 \times 0.1 \times 0.1$ mm) used for data collection was mounted without protection from the air. The cell dimensions were determined from oscillation photographs about the *a* axis and from optimised counter angles for zero- and upper-layer reflections. Data were collected on a Stoe STADI-2 diffractometer with an ω -scan technique in the range $7 < 2\theta < 50^\circ$. The 2710 unique reflections collected from Weissenberg layers (0–10)*kl* having $I > 3\sigma(I)$ were corrected for Lorentz and polarisation effects. Subsequent calculations were carried out with the computer program SHELX [8].

Crystal data: for **1b** $[\text{MoC}_{44}\text{H}_{40}\text{P}_2\text{N}_2\text{O}_4]$. $M = 818.7$, Monoclinic, a 9.582(4), b 22.028(4), c 19.629(2) Å, β 103.65(5)°, U 4026.12 Å³ $Z = 4$, $d_c = 1.35$ cm³ $F(000) = 1688$. Space group $P2_1/c$, $\lambda(\text{Mo-K}\alpha)$ 0.71069 Å, $\mu(\text{Mo-K}\alpha)$ 3.85 cm⁻¹.

The molecular structure (Fig. 1) was solved by conventional Patterson and Fourier difference techniques. Scattering factors were taken from ref. 9. No absorption correction was applied. In the final stages of full matrix least squares refinements all non-hydrogen atoms were given anisotropic thermal parameters. All phenyl rings were treated as rigid bodies with D_{6h} symmetry and C–C distances of 1.395(5) Å. The phenyl hydrogen atoms were included at calculated positions (C–H 1.08(5) Å). Final cycles employed a weighting factor w calculated from $w = k(\sigma^2 F + gF^2)$ where $k = 1.55$ and $g = 0.000408$. Final values of R and R_w ($\{\sum w \|F_o\| - \|F_c\| / \sum w F_o\}$) were 0.0601 and 0.0561. Lists of atomic coordinates and bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre.

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