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DITERTIARY PHOSPHINE COMPLEXES OF (η-ALLYL)DICARBONYL-MOLYBDENUM(II) AND -TUNGSTEN(II)

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Summary

Compounds of the type [$XM(CO)_2(\eta$-allyl)L_2] (where X = Cl and Br; M = Mo and W; L_2 = $Ph_2PCH_2PPh_2$ and $Ph_2PCH_2CH_2PPh_2$) have been prepared from the corresponding MeCN complexes. The spectral properties of these compounds and the effects of chelate ring size on ^{31}P coordination shifts and $J(^{183}W—^{31}P)$ have been investigated.

Introduction

Molybdenum(II) allyl complexes of the type [$XMo(CO)_2(\eta$-allyl)$(MeCN)_2$], where X = Cl and Br, have been shown to undergo allyl elimination reactions with the monodentate ligands PR_3, where R = Ph and n-C_4H_9, with the formation of zero-valent dicarbonyls [$Mo(CO)_2(PR_3)_2(MeCN)_2$] and $(C_3H_5PR_3)^+$ salts [1,2], whereas the bidentate phosphine $Ph_2PCH_2CH_2PPh_2$ has been reported to simply substitute the MeCN molecules in the above complexes [3].

As part of an investigation into the chemistry of η-allyl complexes of the Group VI metals [4,5], a series of ditertiary phosphine complexes of both molybdenum- and tungsten-allyl derivatives have been prepared. The effects of the phosphorus donor atoms and the chelate ring size on the spectral properties of these compounds are reported here.

Experimental

All preparations were carried out under dry nitrogen using solvents and liquid reactants freed from moisture and oxygen by standard procedures. The two phosphines $Ph_2PCH_2CH_2PPh_2$ (dpe) and $Ph_2PCH_2PPh_2$ (dpm) were obtained from commercial sources and recrystallized from ethanol prior to use. Complexes of the type [$XM(CO)_2(\eta$-allyl)$(MeCN)_2$], where X = Cl and Br, and M = Mo and W, were prepared from [$M(CO)_3(MeCN)_3$] by literature methods [6].

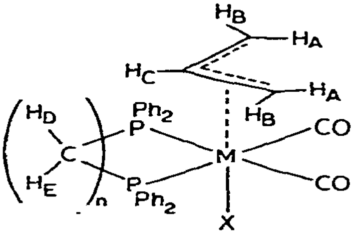

Fig. 1. Stereochemistry of [XM(CO)$_2$(η-allyl)diphosphine] complexes.

as shown in Fig. 1. The allyl group is *trans* to the unidentate anion, the two *cis*-carbonyl groups and the donor atoms of the bidentate ligands are approximately coplanar. The spectroscopic properties of all the complexes listed in Table 1 are consistent with the stereochemistry. The *cis*-carbonyl groups give rise to two strong bands of approximately equal intensity and separated by about 100 cm^{-1}. These bands are generally some 10 cm^{-1} higher than those of corresponding complexes containing bidentate *N*-donors [5], and the increased CO stretching force constants (Table 1) reflect the higher bond order expected for CO groups *trans* to π-bonding ligands. The stretching force constants for the tungsten compounds are about 1% smaller compared with corresponding molybdenum complexes, while increasing the chelate ring size causes a slight but consistent decrease in k(CO).

The effect of ring size is more evident in the ^{31}P NMR spectra. Because of strong ^{1}H—^{31}P couplings, only broad featureless bands were observed under normal scanning procedures. On ^{1}H decoupling, these bands sharpened and revealed satellite peaks in the case of the tungsten complexes due to ^{183}W—^{31}P coupling (Table 2). $J(^{183}$W—^{31}P) values were found to be smaller for the chelated 4-membered ring complexes than for the 5-membered ring systems, as noted for [W(CO)$_4$(diphosphine)] complexes [12,13]. The ^{31}P coordination shifts [δ(complex) — δ(free ligand)] were also analogous to those found in Group VI and VII carbonyl derivatives [12,14], with the larger ring system giving shifts some δ 40 ppm greater than the smaller ring system.

^{1}H NMR showed the three allyl signals with intensity ratios 1 : 2 : 2, although for complexes III, IV, VII and VIII the *meso* proton signals were only partially resolved from ligand CH$_2$ absorptions. On ^{31}P decoupling the allyl spectrum simplified considerably (Fig. 2) and could be interpreted in terms of an AM$_2$X$_2$ spin system. The resolution was not sufficiently high to reveal any coupling between *syn* and *anti* protons, which has been shown to be of the order of 1 Hz for Group VII and VIII allyl complexes [15]. The decoupled spectrum also confirmed the existence of strong coupling between ^{31}P and the *syn* protons of the allyl group (Table 2). Much weaker coupling (estimated at less than 1 Hz) occurred between phosphorus and the *anti* and *meso* protons.

The ^{1}H NMR spectra of compounds I, II, V and VI indicated that the protons of the methylene group of the dpm ligand were non-equivalent by virtue of the different groups above and below the (M—P$_2$) plane. The resulting ABX$_2$ spectrum was readily analysed in all four cases (Table 2), and on ^{31}P decoupling a simple AB quartet was observed. The π-allyl group is expected to exert an aniso-

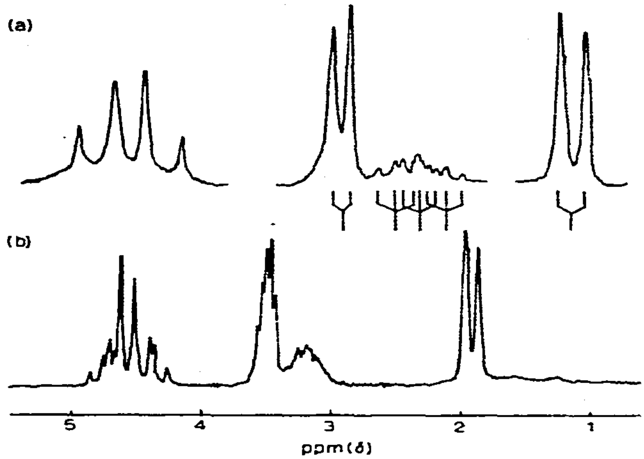

Fig. 2. ^{1}H NMR spectrum of [ClW(CO)$_2$(η-allyl)dpm]: (a) ^{31}P decoupled (X 2 expansion) and (b) normal spectrum.

tropic shielding effect on the closer of the two methylene protons, and consequently the up-field proton signal is assigned to H(D) (Fig. 1). For both tungsten-dmp complexes the up-field methylene proton was more strongly coupled with phosphorus than the downfield proton, but the reverse occurred for the corresponding molybdenum compounds. This could result from a slightly different conformation for the two 4-membered chelate ring systems for the two metals, and would also account for the change in chemical shifts of the H(D) protons on changing from molybdenum to tungsten.

The dpe complexes also contained differently shielded axial and equatorial protons, which gave rise to two complex multiplets centred at about δ 2.3 and 3.0 ppm. On ^{31}P decoupling these signals were expected to analyse as an AA'BB'-spin system. Unfortunately the low solubilities of the dpe complexes resulted in poor quality spectra, and of the 24 lines expected, a maximum of only 8 broad band envelopes were observed.

The 5-membered chelate ring systems formed by bidentate diphosphines have been shown to exhibit a variety of solid state configurations [16], but the energy barriers to conformational inversions in solution are expected to be relatively small. Therefore it seems likely that the observed NMR spectra of the dpe complexes are caused by effective chemical shift differences between non-equivalent methylene protons, rather than their intrinsic chemical shift differences, although it is possible that the ring system is locked in one configuration at room temperature due to steric effects. In an attempt to clarify this point, the NMR spectrum of compound I was examined over the temperature range −60 to +60°C. At low temperatures the ^{31}P decoupled spectrum lost all fine structure and the chemical shift difference between the two methylene proton bands increased slightly. Such an effect is consistent with the existence of two or more rapidly interconverting conformers at room temperature with fairly small energy differences between them, rather than a single fixed configuration for the chelate ring system.

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