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Preliminary communication

OSCILLATIONS OF η^3-ALLYL GROUPS IN PSEUDOOCTAHEDRAL MOLYBDENUM AND TUNGSTEN COMPLEXES

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Summary

The allyl groups in cationic pseudooctahedral complexes of molybdenum and tungsten complexes containing bidentate phosphine ligands undergo oscillations between two potential minima. The fluxional behavior in these $[(\eta^3\text{-C}_3H_5)M(CO)_3(L—L)]^+$ complexes, where L—L = diphos, dppe or dppm, differs from that in neutral analogs, for which pseudorotation of the ligands is observed.

We wish to report the synthesis and characterization of a series of cationic complexes of the general formula $(\eta^3\text{-C}_3H_5)M(CO)_3(L—L)^+PF_6^-$ where M = Mo or W and L—L = the bidentate phosphorus diphos, dppe, or dppm*. These compounds can be synthesized from the recently reported [1] neutral complexes $(\eta^3\text{-C}_3H_5)M(CO)_2(L—L)$ where X = Cl or I by reaction of $AgPF_6$ in the presence of carbon monoxide. Interest in the cationic complexes was stimulated by their dynamic behavior which is unlike that of their neutral precursors.

The addition of $AgPF_6$ to a methylene chloride solution of $(\eta^3\text{-C}_3H_5)Mo(CO)_2$(diphos)Cl saturated with carbon monoxide gave a color change from bright-orange to yellow accompanied by a brown precipitate. Filtration of the crude reaction mixture gave a dark yellow solution which upon addition to cool (0°C), diethyl ether gave a yellow powder. Subsequent isolation and crystallization of the powder gave analytically pure $[(\eta^3\text{-C}_3H_5)Mo(CO)_3(\text{diphos})]PF_6$ as yellow crystals.

Low temperature (<80°C) ^{1}H NMR spectra of $[(\eta^3\text{-C}_3H_5)Mo(CO)_3(\text{dppe})]PF_6$ show that the two ends of the allyl moiety are nonequivalent. The room temperature ^{1}H NMR spectrum (^{31}P-decoupled) shows three resonances for the allyl group of the AA'BB'X spin system characteristic of symmetrical π-allyls. The low temperature ^{1}H NMR spectrum exhibits an ABCDX pattern for the allyl moiety in which cleanly separated resonances for each of the *syn* and *anti* protons are observed.

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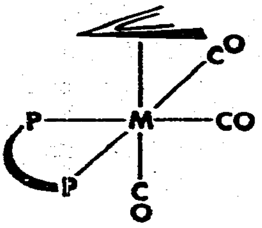
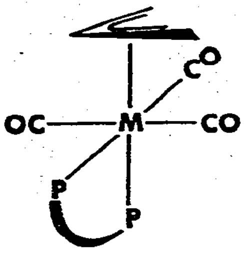
*The abbreviations for the ligands are: bis(diphenylphosphino)ethane = diphos: *cis*-bis(diphenylphosphino)-ethylene = dppe, and bis(diphenylphosphino)methane = dppm.

The room temperature ^{13}C NMR spectra of $[(\eta^3\text{-}C_3H_5)Mo(CO)_3(\text{diphos})]PF_6$ show two carbonyl carbon resonances of intensity ratio two to one. The carbonyl carbon resonance of intensity two is an apparent triplet with ^{31}P—^{13}C splitting of 8.4 Hz. The resonance of intensity one appears as a doublet of doublets with ^{31}P—^{13}C splitting of 9.8 and 23.8 Hz. Of the two possible configurations shown below, structure II is more consistent with the ^{13}C NMR data. The position of the three carbonyls with respect to the phosphorus nuclei can be deduced from the ^{31}P—^{13}C coupling of the carbonyl carbons in the ^{13}C NMR spectrum. In the analogous system, $(CO)_4Mo(\text{diphos})$, Randall et al. [2] have observed that the *trans*-^{31}P—^{13}CO coupling is two to three times larger than the *cis*-^{31}P—^{13}CO coupling. The data supports a structure, such as II, in which two of the carbonyls are equivalent and split *cis* coupling to phosphorus, while the remaining carbonyl exhibits both *cis* and *trans* splitting by phosphorus. This preference for structure II with diphos contrasts with diamine ligands in which structure I is preferred [3].



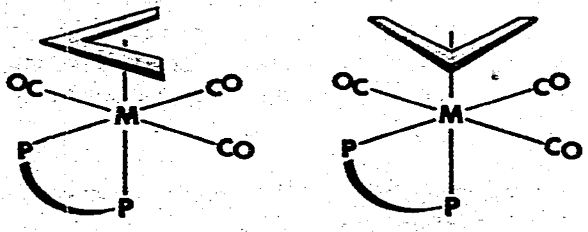
I



II

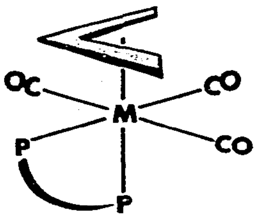
The ^{31}P NMR spectra at room temperature of the $[(\eta^3\text{-}C_3H_5)M(CO)_3(L\text{—}L)]PF_6$ complexes show two (or four lines depending on the resolution of ^{31}P—^{31}P splitting) lines of equal intensity.

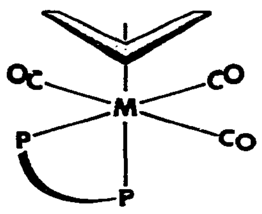
The appearance of separate resonances for certain carbonyl carbons in the ^{13}C NMR spectra and the phosphorus nuclei in the ^{31}P NMR spectra at room temperature indicates that the tricarbonyl bisphosphine framework is rigid. This is unlike the neutral $(\eta^3\text{-}C_3H_5)M(CO)_2(L\text{—}L)X$ complexes in which the phosphorus atoms and halogen effectively execute a trigonal twist rearrangement [1]. The dynamic ^{1}H NMR spectra for the cations, however show that the allyl moiety is nonrigid. A rearrangement consistent with the data thus far presented is shown below.



The mechanism may be described as an allyl rotation in which the allyl group rotates between two or four possible minima above the equatorial plane formed by the three carbonyls and the phosphorus atom. The appearance of two sets of *syn* and *anti* proton signals and one central proton signal, all of equal intensity, in the limiting low temperature ^{1}H NMR spectrum indicates that the allyl oscillates between two positions related by a mirror plane. That is, the potential wells for the two enantiomeric conformers are equivalent and the molecule can be accurately described as fluxional. The potential minima are assumed to bisect the bonds to the equatorial ligands by analogy to the structure of the halide in the crystal [1]. The minima for A and A′ are at least 3 kcal/mol lower in energy than B and B′ because no evidence of more than a single pair of enantiomers is found.

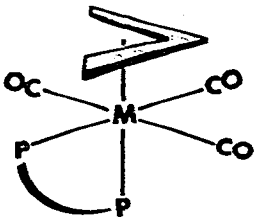
A

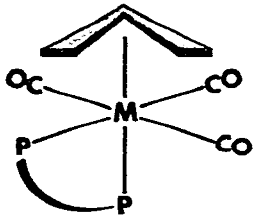




A′

B





B′

The ^{13}C NMR spectra are also consistent with the interpretation of an oscillation of the allyl group. For example, in $[\eta^3\text{-}C_3H_5Mo(CO)_3(dppm)]PF_6$ at −89°C in CH_2Cl_2 two terminal allyl carbon resonances are observed at δ 60.34 and 51.31 ppm; furthermore, three carbonyl carbon resonances are found at δ 204.40, 206.54 and 216.26 ppm. These resonances average to produce a single terminal carbon resonance at δ 57.17 ppm and carbonyl resonances in a ratio of 2/1 at δ 206.32 and 217.45 ppm. Phosphorus coupling is only resolved in the high temperature carbonyl spectra, where the resonance of intensity one is a doublet of doublets ($J(P\text{—}C_{cis})$ 5.6 Hz and $J(P\text{—}C_{trans})$ 24.6 Hz) and the other is a triplet ($J(P\text{—}C_{cis})$ 7.9 Hz).

That the allyl motion is indeed a rotation and not a σ—π—σ rearrangement can be shown from spin saturation transfer experiment [4]. Irradiation of the *anti* proton in site 1 caused a drop in intensity of the *anti* proton in site 2, with no change in the intensity of the *syn* protons in sites 3 and 4. Partial saturation of the *syn* proton of site 4 caused a decrease in intensity of the *syn* proton in site 3 with no change in the intensity of the *anti* protons 1 and 2. This implies that exchange occurs between *syn* protons and *anti* protons, respectively, but not between the *syn* and *anti* protons. A σ—π—σ pathway, therefore, is not significant since this mechanism would require interchange of *syn* and *anti* protons*.

The data does not allow a distinction between a clockwise rotation of 90° and a counterclockwise rotation of 270°. The barriers for these processes may depend upon the interaction of the allyl protons with one of the phenyl rings of the equatorial phosphorus atom assuming a geometry analogous to $(\eta^3\text{-C}_3\text{H}_5)\text{Mo(CO)}_2\text{(diphos)Cl}$. Upfield shifts of up to 213 Hz of the central proton of the allyl have been observed for the tungsten derivatives $(\eta^3\text{-C}_3\text{H}_5)\text{W(CO)}_2\text{(L—L)X}$ presumably due to the proximity of the phenyl ring creating unusual shielding effects.

It is noteworthy that the introduction of localized charge upon the metal atom has drastically altered the dynamics of the system. A dramatic change in the rate of isomer interconversion was noted upon conversion of the neutral $(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_2\text{-}\eta^3\text{-C}_3\text{H}_5$ to the cationic $(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)(NO)-}\eta^3\text{-C}_3\text{H}_5$ derivatives [5].

In Table 1 are summarized the analytical and physical data for some molybdenum and tungsten cations.

A comprehensive discussion of the NMR spectra as well as nucleophilic additions and π-olefin complexes derived from the cations will be forthcoming.

TABLE 1

ANALYTICAL AND PHYSICAL DATA FOR SOME MOLYBDENUM AND TUNGSTEN COMPLEX CATIONS

Compound	Color	M.p. (°C)	Analysis (Found (calcd.) (%))	
			C	H
$[(\eta^3\text{-C}_3\text{H}_5)\text{Mo(CO)}_3\text{(diphos)}]\text{PF}_6$	yellow	152	50.24 (50.27)	3.85 (3.80)
$[(\eta^3\text{-C}_3\text{H}_5)\text{Mo(CO)}_3\text{(dppe)}]\text{PF}_6$ [a]	pale yellow	191	47.27 (46.76)	3.49 (3.42)
$[(\eta^3\text{-C}_3\text{H}_5)\text{Mo(CO)}_3\text{(dppm)}]\text{PF}_6$	yellow	144	49.69 (49.60)	3.78 (3.60)
$[(\eta^3\text{-C}_3\text{H}_5)\text{W(CO)}_3\text{(diphos)}]\text{PF}_6$	pale yellow	173	45.34 (45.12)	3.63 (3.41)
$[(\eta^3\text{-C}_3\text{H}_5)\text{W(CO)}_3\text{(dppe)}]\text{PF}_6$	pale yellow	178	45.18 (45.23)	3.59 (3.18)
$[(\eta^3\text{-C}_3\text{H}_5)\text{W(CO)}_3\text{(dppm)}]\text{PF}_6$ [a]	yellow	188	41.97 (41.64)	3.30 (3.15)

[a] Crystallize with $1\text{CH}_2\text{Cl}_2$.

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*The proton chemical shifts for $(\eta^3\text{-C}_3\text{H}_5)\text{Mo(CO)}_3\text{(dppe)}^+$ at −108°C in $\text{C}_3\text{D}_6\text{O}$ are: δ 2.62 and 3.23 (*anti*); 4.24 and 4.31 (*syn*); and 6.31 (central) ppm. The most convenient separations for saturation transfer experiments were found in $(\eta^3\text{-C}_3\text{H}_5)\text{W(CO)}_3\text{(dppm)}^+$ at −85°C for which shifts of δ 2.82 (1,*anti*); 3.26 (2,*anti*); 3.48 (3,*syn*); 3.67 (4,*syn*); and 6.22 ppm (central) were found. All of the complexes rearrange with a $\Delta G^* \sim 10$ kcal/mol.

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