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PREPARATION OF SOME COMPLEXES OF THE TYPE $(C_6H_5)_3P[(CH_3)_2AsCH_2CH(R)CH_2As(CH_3)_2]M(CO)_3$ (M = Mo or W, R = H or $C(CH_3)_3$)

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Summary

The title compounds, which contain six-membered chelate rings locked in the chair conformation, have been prepared by the reaction of $(C_6H_5)_3P$ with the appropriate tetracarbonyl derivative in refluxing mesitylene.

Introduction

Recently from these laboratories the preparation of chelate complexes of the type $(L—L)M(CO)_4$ (L—L = ditertiary arsine, M = Cr, Mo or W) and $(L—L)Mn(CO)_3X$ (X = halogen) have been described [1-5]. Of particular interest have been the complexes containing six-membered chelate rings, where, by using NMR techniques, it was possible to determine the conformation of the chelate ring in solution [4, 5].

For the compounds with L—L = $(CH_3)_2As(CH_2)_3As(CH_3)_2$ (I) and M = Cr, Mo and W, the chelate ring was found to be undergoing rapid interconversion between the two possible chair forms. In the manganese derivatives of I the ring was found to be locked. When L—L contained the bulky t-butyl group as in $(CH_3)_2AsCH_2CH(C(CH_3)_3)CH_2As(CH_3)_2$ (II) all the compounds had locked chair conformations.

As part of continuing studies on the factors affecting chelate ring conformations we report the preparation of some triphenylphosphine derivatives $(C_6H_5)_3P(L—L)M(CO)_3$, M = Mo or W, L—L = I or II.

Experimental

Mesitylene was dried using sodium, other hydrocarbon solvents using CaH_2, and dichloromethane using P_2O_5. The tetracarbonyl derivatives were prepared as

previously described [4]. Commercially available triphenylphosphine was recrystallized from CH_2Cl_2/n-heptane before use. All chromatographic separations were done on Florisil columns.

Infrared spectra (Table 1) were recorded on a Perkin—Elmer 457 instrument. The NMR spectra were usually recorded using a Varian T60 spectrometer. The spectrum of $(C_6H_5)_3P[(CH_3)_2AsCH_2CH(C(CH_3)_3)CD_2As(CH_3)_2]Mo(CO)_3$ was obtained using Varian HA-100 and XL-100 instruments; the latter operating in the Fourier transform mode. The final NMR parameters for this compound were obtained using the iterative LAOCOON 111 program modified for use on the U.B.C. IBM 360-67 computer.

Microanalytical data (Table 1) were obtained by Mr. Peter Borda of this department.

Preparation of $(C_6H_5)_3P[(CH_3)_2As(CH_2)_3As(CH_3)_2]Mo(CO)_3$

A solution of $[(CH_3)_2As(CH_2)_3As(CH_3)_2]Mo(CO)_4$ (0.68 g, 1.47 mmol) and $P(C_6H_5)_3$ (3.0 g, 11.5 mmol) in mesitylene was refluxed under N_2 for 3h. The solution was allowed to cool and chromatographed using a mixture of petroleum ether (b.p. 30-60°) and benzene (1:1) to elute mesitylene and triphenylphosphine. The column was then eluted with benzene (or dichloromethane) to give the crude product $(C_6H_5)_3P[(CH_3)_2As(CH_2)_3As(CH_3)_2]Mo(CO)_3$ (0.85 g, 87%). The analytical sample was obtained by recrystallisation from benzene-heptane (under nitrogen).

When the crude material was washed with n-heptane there was evidence for trace amounts of a more soluble yellow by-product which had an infrared spectrum, in the CO stretching region, expected for the *mer*-isomer (1967 (w), 1863 s cm^{-1}).

The tungsten analogue $(C_6H_5)_3P[(CH_3)_2As(CH_2)_3As(CH_3)_2]W(CO)_3$ was prepared similarly only with a reaction time of 43 h.; the yield was somewhat lower (77%).

The same method was used for the t-butyl derivatives $(C_6H_5)_3P[(CH_3)_2AsCH_2CH(C(CH_3)_3)CH_2As(CH_3)_2]M(CO)_3$ (M = Mo or W) with reflux times of 4 h. (for Mo) and 7 days (for W).

Preparation of $(C_6H_5)_3[(CH_3)_2AsCH(C(CH_3)_3)CD_2As(CH_3)_2]Mo(CO)_3$

A solution of $[(CH_3)_2AsCH_2CH(C(CH_3)_3)CD_2As(CH_3)_2]Mo(CO)_4$ (0.80 g, 1.59 mmol) and $P(C_6H_5)_3$ (3.0 g, 11.5 mmol) in mesitylene (25 ml) was refluxed under N_2 for 4 h. The resulting solution was placed on a column of Florisil and eluted with benzene/petroleum ether (b.p. 30—60°) to remove mesitylene and $P(C_6H_5)_3$. The column was then eluted with dichloromethane to give the crude, yellow product $(C_6H_5)_3P[(CH_3)_2AsCH_2CH(C(CH_3)_3)CD_2As(CH_3)_2]Mo(CO)_3$ (1.10 g, 94%).

This was dissolved in hot solvent (benzene (40 ml) and n-heptane (70 ml)). The resulting solution was filtered and placed in a refrigerator at —15° for 2 h. The crystals (ca. 0.6 g) thus obtained were recrystallized from benzene/n-heptane. Finally the product was recrystallized from dichloromethane/n-heptane to give white crystals (0.15 g first crop) of a pure isomer of $(C_6H_5)_3P[(CH_3)_2AsCH_2CH(C(CH_3)_3)CD_2As(CH_3)_2]Mo(CO)_3$ (m.p. 164-166°). This isomer had NMR resonances (CH_2Cl_2 solution) at δ 1.41, 0.93 and 0.55 ppm.

An NMR-spectrum of this compound, in the region δ 3.0-0.0 ppm downfield from TMS is shown in Fig. 2. To obtain accurate chemical shifts the ABX part of the spectrum was enhanced using the XL-100 spectrometer operating in the Fourier transform mode. The ABX spectrum was fitted making the assumption that part of spectrum was hidden by other resonances. There is thus some uncertainty in the parameters listed in Table 2 although they are reasonable when compared with similar systems.

Results and Discussion

The complexes $(C_6H_5)_3P[(CH_3)_2AsCH_2CHRCH_2As(CH_3)_2]M(CO)_3$ (M = Mo or W, R = H or $C(CH_3)_3$) have been prepared by the reaction of the corresponding tetracarbonyl with triphenylphosphine in refluxing mesitylene (eq. 1). Analytical data for the new complexes are given in Table 1.

$$(L{-}L)M(CO)_4 + (C_6H_5)_3P \rightarrow (C_6H_5)_3P(L{-}L)M(CO)_3 + CO \qquad (1)$$

L—L = I or II, M = Mo or W.

As is usual with substitution reactions of Group VI carbonyls the molybdenum complex formed faster than the tungsten analogue. The chromium complex did not form under the same conditions. The reactions do not go to completion when carried out in sealed Carius tubes at temperatures of 190°. Presumably the build up of CO prevents further reaction.

Dobson and Houk [6] found that similar drastic conditions were needed to prepare L(diphos)Mo(CO)$_3$ from (diphos)Mo(CO)$_4$ (diphos = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$). L needed to be a ligand with good π-acceptor properties, and in no case investigated was the chelating ligand displaced. We have found some evidence for *trans*-$[(CH_3O)_3P]_2W(CO)_4$ as one of the products from the reaction of $(CH_3O)_3P$ with $[(CH_3)_2As(CH_2)_3As(CH_3)_2]W(CO)_4$.

The pattern of the infrared spectra of the compounds prepared in this investigation (Table 1) supports the *fac* configuration. This pattern is also similar to that obtained from the complexes $(L{-}L)Mn(CO)_3X$ (L—L = I, X = Cl or $GeCl_3$) which have known solid state structures [7, 8].

Dobson and Houk [6] found that the geometry of the product seems to depend on the steric requirements of both the incoming ligand and the chelate [6]. For example, $(C_6H_5)_3P$ gives *mer*-L(diphos)Mo(CO)$_3$ yet $(C_6H_5)_3Sb$ and CH_3CN afford the *fac* isomer. Thus, not unexpectedly, the steric requirements of the ditertiary arsines used in the present investigation appear to be less than those of diphos with its $P(C_6H_5)_2$ moieties. Only a trace of the *mer* isomer seems to be produced when $(C_6H_5)_3P$ reacts with $(L{-}L)Mo(CO)_4$ (L—L = I).

The NMR spectrum of $(C_6H_5)_3P(L{-}L)M(CO)_3$ (L—L = I) shows two As—CH_3 resonances consistent with the *fac* geometry (Table 1). In both compounds one of these resonances shows a large upfield shift compared with a normal As—CH_3 signal. These may be assigned to the methyl groups closer to the phenyl rings of the $P(C_6H_5)_3$ group. Similar upfield shifts of methyl groups in close proximity to phenyl groups have been observed before [9, 10].

The six-membered ring in the complex $(L{-}L)Mn(CO)_3Cl$ (L—L = I) is locked with the structure A (M = Mn, X = Cl, Y = CO, R = H), repulsion between

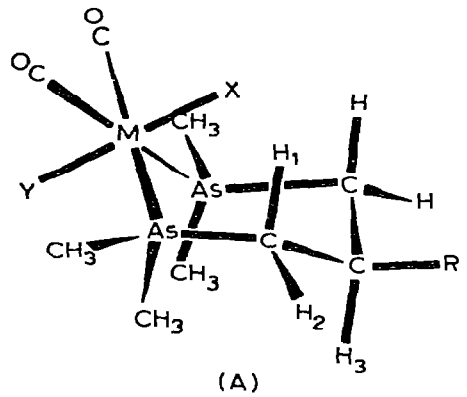
TABLE 1

ANALYTICAL AND SPECTROSCOPIC DATA FOR NEW COMPLEXES

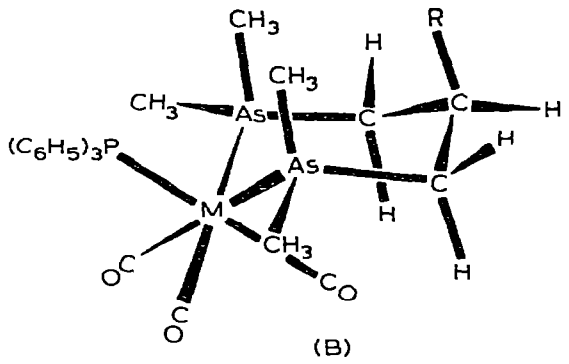
Compound[a]	Analysis found (calcd.) (%)		ν(CO) (cm^{-1})[b]			^1H NMR[d]		
	C	H				As–CH_3		$C(CH_3)_3$
$(C_6H_5)_3P[(CH_3)_2As(CH_2)_3As(CH_3)_2]Mo(CO)_3$	48.33 (48.43)	5.00 (4.79)	1947	1858(sh)	1852	1.39	0.55	
$(C_6H_5)_3P[(CH_3)_2As(CH_2)_3As(CH_3)_2]W(CO)_3$	42.88 (43.02)	4.28 (4.25)	1941	1853	1846	1.55	0.57	
$(C_6H_5)_3P[(CH_3)_2AsCH_2CH(C(CH_3)_3)CH_2As(CH_3)_2]Mo(CO)_3$[c]	52.30 (52.17)	5.90 (5.61)	1949	1859(sh)	1853	1.41, 1.38	0.55	0.93, 0.88
$(C_6H_5)_3P[(CH_3)_2AsCH_2CH(C(CH_3)_3)CH_2As(CH_3)_2]W(CO)_3$[c]	46.86 (46.01)	5.25 (5.01)	1941	1853	1847	1.50, 1.55	0.63, 0.59	0.95, 0.90

[a] All compounds are pale-yellow. [b] Cyclohexane solution, all bands are strong. [c] Mixture of isomers. [d] All compounds show multiplets at δ ~7.5 ppm [$(C_6H_5)_3P$] and weak multiplets at ~1.0 ppm due to the $-CH_2-CHR-CH_2-$ fragment. Chemical shifts are in ppm downfield from external TMS. The solvent is CH_2Cl_2.

the axial chlorine atom and the arsenic methyl groups seem to be responsible for



(A)



(B)

this effect [5, 7]. (The corresponding complexes (L—L)$M(CO)_4$ (M = Cr, Mo, W) are not locked [4]). It is therefore fairly certain that the complexes $(C_6H_5)_3P$-(L—L)$M(CO)_3$ (L—L = I) are also locked because of repulsion between the triphenylphosphine ligand and the arsenic methyl groups, and they probably have the structure A with M = Mo or W, X = $(C_6H_5)_3P$ and R = H.

Fig. 1 shows an NMR spectrum in the As—CH_3 regions of $(C_6H_5)_3P$(L—L)W-$(CO)_3$ (L—L = II). The two singlets present for both inequivalent arsenic methyl groups and the t-butyl group clearly show the presence of two isomers. This spectrum is obtained from a sample recrystallized from benzene/n-heptane. Attempts to separate the two compounds by chromatography were unsuccessful. This was probably due to isomerization on the Florisil as was found for the molybdenum analogues. This process which involves breaking As—Mo (or W) bonds during chromatography has been observed in other systems [11]. The analogous (L—L)$Mn(CO)_3X$ isomers convert to the more stable one on heating [5]; the isomerism is due to the orientation of the t-butyl group relative to the axial ligand on the metal i.e. their orientation can be *cis* or *trans*.

In the case of isomers of $(C_6H_5)_3P$(L—L)$Mo(CO)_3$ (L—L = II), it was possible to isolate one isomer in a pure state by fractional crystallization. Part of the NMR spectrum of this isomer is shown in Fig. 2. The ABX spectrum of the

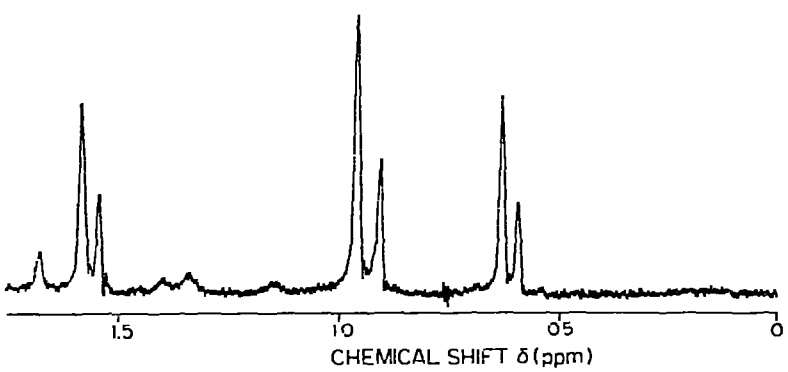


Fig. 1. Partial NMR spectrum of the isomers of $(C_6H_5)_3P[(CH_3)_2AsCH_2CH(C(CH_3)_3)CH_2As(CH_3)_2]W(CO)_3$ in CH_2Cl_2 showing the two sets of resonances for the arsenic methyl and t-butyl groups.

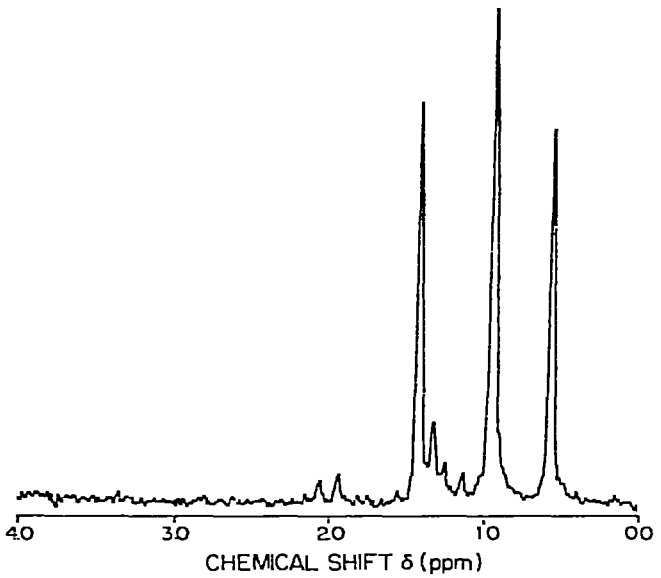


Fig. 2. Partial deuterium decoupled NMR spectrum in $CDCl_3$ of the pure isomer of $(C_6H_5)_3P[(CH_3)_2AsCH_2CH(C(CH_3)_3)CD_2As(CH_3)_2]Mo(CO)_3$ showing the arsenic methyl and t-butyl resonances and the ABX pattern of the $-CH_2CH-$ moiety.

bridging protons is partially obscured by both As—CH_3 and t-butyl resonances. However, it is possible to obtain a reasonable solution of the spectrum, and the results are indicated in Table 2. The vicinal coupling constants indicate that the chelate ring is locked with the t-butyl group in the equatorial position. Thus J_{13} and J_{23} are very similar to those obtained from other octahedral (L—L)$M(CO)_4$ and (L—L)$Mn(CO)_3X$ complexes (L—L = II) [4, 5] (Table 2), although it is difficult to compare absolute values of these coupling constants.

Since the isomer actually isolated is the one formed in greater yield it probably has the least sterically hindered structure i.e. it has structure A with M = Mo, X = $P(C_6H_5)_3$, Y = CO and R = $C(CH_3)_3$. In these chelate rings it is usual to find the chemical shift of the axial proton well upfield of the equatorial one on the same carbon atom. This is seen for example, in the second and fourth entry in Table 2. However when X is halogen [5] or $GeCl_3$ [8] the chemical shift difference is much smaller and indeed the axial chemical shift can be downfield of the equatorial. This effect is seen in the third entry in Table 2. The downfield shift

TABLE 2

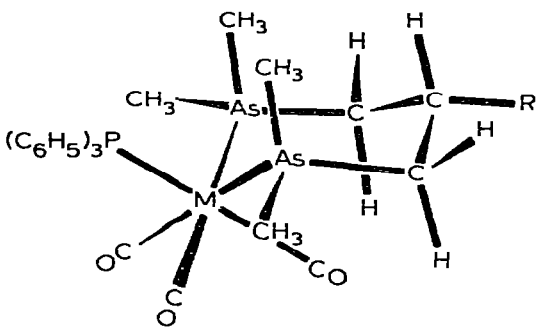
SOME NMR PARAMETERS OF X(L—L)$M(CO)_3$ COMPLEXES (L—L = II)[a]

M	X	Y	δ_1	δ_2	δ_3	J_{12}	J_{13}	J_{23}
Mo	$(C_6H_5)_3P$	CO	1.386	2.235	1.642	−12.7	12.1	0.6
Mo[b]	CO	CO	1.136	2.084	1.174	−12.4	11.3	0.8
Mn[c]	Br	CO	1.863	1.913	1.246	−12.4	11.0	2.4
Mn[c]	CO	Br	1.32	2.176	1.886	−12.4	11.6	2.1

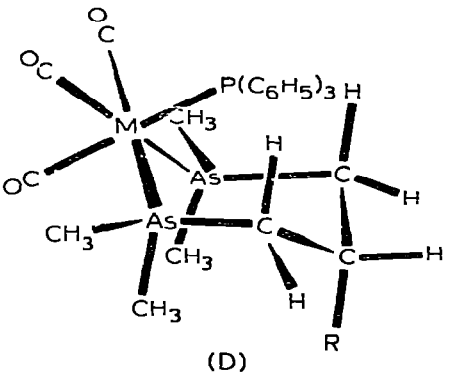
[a] The numbers and letters refer to A. Couplings are in Hz and chemical shifts in ppm downfield from TMS. The solvent is $CDCl_3$. [b] From ref. 4. [c] From ref. 5.

has been ascribed to an interaction between X and the axial hydrogen atom. In the case of $(C_6H_5)_3P(L{-}L)Mo(CO)_3$ (L—L = II) this effect is not seen, however, it could be masked by an upfield shift due to the proximity of the phenyl rings on the triphenylphosphine.

The configuration of the other isomer is of interest. There are three remaining possible chair configurations indicated in B, C, and D. B has *cis* axial methyl



(C)



(D)

and t-butyl groups and is unlikely since it could easily convert to the more stable isomer already described, by chair→chair interconversion. C has axial methyls adjacent to the triphenyphosphine but an equatorial t-butyl group. D has an axial t-butyl group which will interact strongly with the *cis* axial methyls but it also has equatorial arsenic methyl groups to interact with the triphenylphosphine. It would seem at first sight that the repulsions in C would be less than than in D. C has an equatorial t-butyl group which is indicated by the NMR spectrum of the mixture of isomers since the X part of the ABX pattern of both isomers is similar, each consisting of a doublet which indicates that J_{13} is small. However, C has axial methyl groups in close proximity to the phenyl rings. This should result in a considerable difference in chemical shift for the arsenic methyl groups for the isomers. As can be seen from Table 1 this is not so. Thus the evidence is conflicting and no firm decision can be made. The two isomers of $(L{-}L)Mn(CO)_3Br$ (L—L = II) have the t-butyl group equatorial and differ in the axial—equatorial arrangement of the arsenic methyl groups [5] (A, M = Mn, X or Y = CO or Br, R = t-butyl).

Finally it was observed that reaction 1 (M = W) was much faster when R = H. If an S_N2 mechanism is assumed this difference can be explained on the basis of the steric effect of the t-butyl group. The starting material $(L{-}L)W(CO)_4$ (L—L = II) has two permanent axial arsenic methyls which would hinder attack on that side in addition to the bulky t-butyl group which would hinder attack on its side. The ligand with R = H would not be subjected to these restrictions. A lowering of the rate constant by substituents remote from the metal centre has been observed before [12].

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