Evidence for the Interaction of Trimethylalane with the Oxygen Atom of a Terminal Metal Carbonyl Group

By JOHN C. KOTZ* and CARL D. TURNIPSEED

(*Department of Chemistry, Kansas State University, Manhattan, Kansas* 66502)

Summary The presence of a CO stretching frequency at 1665 cm^{-1} in the i.r. spectrum of the 1 : 1 complex formed between trimethylalane and triphenylphosphoniumcyclopentadienylidemolybdenum tricarbonyl suggests co-ordinate covalent bonding between aluminium and the oxygen atom of one of the terminal carbonyl groups.

ALTHOUGH carbon monoxide formally has lone pairs of electrons on both the carbon and oxygen atoms, until recently there was no evidence that the oxygen lone pair could be utilized in forming a co-ordinate covalent bond even though theoretical calculations indicated that this should be possible.[1] However, Shriver and his co-workers recently reported that $(\pi\text{-}C_5H_5)_2Fe_2(CO)_4$ and triethylalane give a 1 : 2 complex; preliminary *X*-ray studies indicate that one molecule of alane is bonded to each of the bridging carbonyl groups.[2] Their communication prompts us to report our findings on the interaction of trimethylalane with triphenylphosphoniumcyclopentadienylidemolybdenum tricarbonyl,[3] $Ph_3PC_5H_4Mo(CO)_3$ [henceforth called cpylid $Mo(CO)_3$].

An excess of Al_2Me_6 was distilled from a vacuum-line into a flask containing about 1 mmole of cpylid $Mo(CO)_3$ and 10—20 ml of toluene.† Although 1 mmole of cpylid

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† Preparations of the alane complex and samples for n.m.r. experiments, as well as tensimetric titrations and alcohol reactions, were carried out on a vacuum line of standard design. Toluene was distilled from sodium, stored over molecular sieves on the vacuum line, and then stirred with CaH_2 for several hours before use. Air-sensitive solids and solutions were handled in a nitrogen-filled dry-box which was equipped with drying and deoxygenating columns.

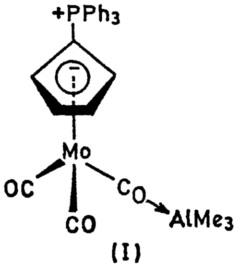
$Mo(CO)_3$ does not completely dissolve in this amount of toluene at room temperature, addition of the alane caused it to dissolve readily to give a dark brown solution. When hexane was added, a brown solid precipitated. The solid could be recrystallized by dissolving it in 30—50 ml of dry toluene, filtering the solution rapidly, and then quickly reprecipitating it with hexane. If this operation was carried out more than twice, the i.r. spectrum of the recovered material indicated the presence of unreacted cpylid $Mo(CO)_3$; continual washing with dry toluene ultimately gave pure starting material.

Two methods of analysis indicated that the solid was the 1 : 1 complex cpylid $Mo(CO)_3{\cdot}AlMe_3$. Treatment of the recrystallized solid with ethanol produced 3 moles of methane per formula weight. Tensimetric titrations of the complex with NMe_3 indicated a 1 : 1 reaction. Most importantly, the solid isolated from the alcohol and amine reactions was pure cpylid $Mo(CO)_3$, and $Me_3N{\cdot}AlMe_3$ could be isolated upon fractionation of the volatile materials from the amine titrations. The molecular weight could not be determined because of dissociation in solution (*vide infra*). The 2100—1600 cm^{-1} region of the i.r. spectra of both the parent metal carbonyl and the complex is shown in the Figure; the remainder of the spectrum of the alane complex is similar to that of cpylid $Mo(CO)_3$ except for three bands due to co-ordinated $AlMe_3$ at 1180, 690, and 615 cm^{-1}. While the bands at 1932 and 1845 cm^{-1} are in a region typical of terminal carbonyl groups, the intense band at 1665 cm^{-1} is much lower than normal terminal or bridging metal carbonyl frequencies. Shriver reported that the bridging CO frequency decreased 112 cm^{-1} to 1682 cm^{-1} upon formation of the complex $cp_2Fe_2(CO)_4{\cdot}2AlEt_3$.[2] Hence it is reasonable to suggest structure (I) for cpylid $Mo(CO)_3{\cdot}AlMe_3$.

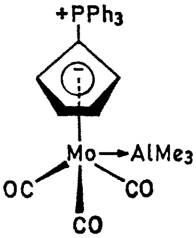
FIGURE. (*I.r. spectra of* cpylid $Mo(CO)_3$ *and* cpylid $Mo(CO)_3{\cdot}AlMe_3$ *as Nujol mulls) in the carbonyl stretching region.*

Shriver also reported that the terminal CO frequencies for $cp_2Fe_2(CO)_4{\cdot}2AlEt_3$ increased about 40 cm^{-1}. A similar high-frequency shift for the non-complexed CO groups was observed for cpylid $Mo(CO)_3{\cdot}AlMe_3$, thus indicating an increase in the triple bond character of these CO groups and a concomitant decrease in basicity of the oxygen lone pair. This observation suggests an explanation for the fact that only a 1 : 1 complex was isolated.

We had previously found that H^+ or BF_3 form complexes with cpylid $Mo(CO)_3$ wherein the metal is apparently the basic site.[4] Compound (II) was therefore the expected product of the alane reaction; however, the 1665 cm^{-1} band apparently rules it out. The reason for the utilization of different basic sites by different Lewis acids is not known. However, $cp_2Fe_2(CO)_4$ also apparently adds a proton at the metal.[4]



(I)



(II)

Since a bridging CO group more closely resembles an organic carbonyl group than does a terminal group, it is reasonable that bridging groups should be more basic than terminal groups. Thus, alane complexes involving bridging groups should show less tendency to dissociate in solution than complexes such as (I). Indeed, Shriver[2] reported that n.m.r. spectra and molecular weights could be obtained for his complexes, while we observed that successive recrystallizations (*vide supra*) of cpylid $Mo(CO)_3{\cdot}AlMe_3$ led to dissociation. Furthermore, we found that cpylid $Mo(CO)_3$ could not be dissolved in small amounts of toluene except in the presence of an excess of Al_2Me_6. These latter observations suggest the equilibrium

$$2\ \text{cpylid}\ Mo(CO)_3 + Al_2Me_6 \rightleftharpoons 2\ \text{cpylid}\ Mo(CO)_3{\cdot}AlMe_3$$

Such an equilibrium may account for the fact that rapid exchange of bridging and terminal methyl groups was found to occur (by n.m.r. spectroscopy) in toluene solutions of cpylid $Mo(CO)_3{\cdot}AlMe_3/Al_2Me_6$ even at −80°, a temperature well below the coalescence temperatn for Al_2Me_6.

Shriver noted that his "results introduce a new structural feature in carbonyl chemistry and indicate that Lewis basicity may be a general property of the bridging carbonyl ligand."[2] Our finding that terminal metal carbonyl ligands, which even more closely resemble carbon monoxide, also function in this manner broadens the implications of this statement.

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[1] K. F. Purcell, *J. Amer. Chem. Soc.*, 1969, **91**, 3487; *cf.* ref. 17 therein.
[2] N. J. Nelson, N. E. Kime, and F. Shriver, *J. Amer. Chem. Soc.*, 1969, **91**, 5173.
[3] E. W. Abel, A. Singh, and G. D. Wilkinson, *Chem. and Ind.*, 1959, 1067.
[4] J. C. Kotz and D. G. Pedrotty, *Organometallic Chem. Rev.*, 1969, **4**, 479.