Journal of Organometallic Chemistry, 78 (1974) C29—C30

Preliminary communication

THE PREPARATION OF $(\pi\text{-}C_5H_5)Mo(COCH_3)(CO)_2As(C_6H_5)_3$

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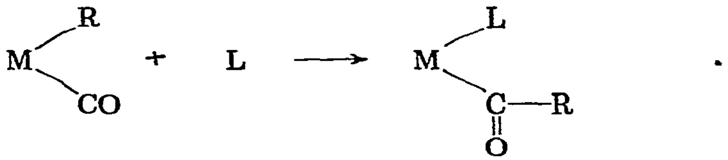
(Received July 22nd, 1974)

Summary

The reaction of $(\pi\text{-}C_5H_5)Mo(CO)_3CH_3$ with $As(C_6H_5)_3$ in acetonitrile at 35° C gives the title compound.

Carbon monoxide insertion reactions of the type



have been reported for a large number of σ-bonded ligands (R). metals (represented as M to include ancillary ligands) and incoming ligands (L) [1]. However, synthetic and mechanistic investigations have concentrated largely on phosphorus ligands. In the case of $(\pi\text{-}C_5H_5)Mo(CO)_3CH_3$ Craig and Green [2,3] have reported kinetic data for the reaction with phosphorus ligands [4,5] in various solvents, but have stated that there is no reaction with corresponding arsenic, sulphur or nitrogen ligands. This is surprising in view of the reaction of $CH_3Mn(CO)_5$ with $As(C_6H_5)_3$ [6—8], but is analogous to the findings for $(\pi\text{-}C_5H_5)Fe(CO)_2CH_3$ [9]. The failure of arsenic ligands to give an acetylmolybdenum complex, even in the most favourable solvent, acetonitrile, was explained in terms of a kinetic effect [2,3]. The overall methyl migration reaction was proposed to proceed via an intermediate which is reactive towards phosphorus ligands but unreactive towards other ligands and was correlated with nucleophilicity.

A preliminary reaction between $(\pi\text{-}C_5H_5)Mo(CO)_3CH_3$ and $As(C_6H_5)_3$ in acetonitrile under N_2, monitored by IR sampling, showed the appearance of a new band at 1600 cm^{-1}, which is typical of an acetyl group bonded to a

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transition metal [1]. The reaction was slow at room temperature but quite rapid at 35°C and went almost to completion. The reaction on a preparative scale, $(\pi\text{-}C_5H_5)Mo(CO)_3CH_3$ (2.5 mmol) in acetonitrile (10 ml) added to $As(C_6H_5)_3$ (5 mmol) in acetonitrile (10 ml) and the mixture stirred for 24 hours at room temperature and then heated to 35°C for 3 hours, gave a yellow-brown solid when the solution was taken to dryness. Recrystallisation of the solid from dichloromethane—hexane mixtures gave yellow crystals of $(\pi\text{-}C_5H_5)Mo(COCH_3)(CO)_2As(C_6H_5)_3$ (Found: C, 57.35; H, 4.17; N, 0.00. $C_{27}H_{23}AsMoO_3$ calcd.: C, 57.27; H, 4.10; N, 0.0%.), which melted under vacuum at 118°C, with a yield of 26%. The IR and NMR data (Table 1) are remarkably similar to the corresponding triphenylphosphine complex.

TABLE 1

IR (2200—1500 cm^{-1}) AND NMR DATA FOR $(\pi\text{-}C_5H_5)Mo(COCH_3)(CO)_2L$ COMPLEXES

L	IR [a]		NMR [b]
$As(C_6H_5)_3$	1940s 1860vs	terminal CO	7.37 acetyl protons 4.96 $\pi\text{-}C_5H_5$ protons
	1600m	acetyl CO	2.4—2.7 phenyl protons
$P(C_6H_5)_3$ [c]	1943s 1858vs	terminal CO	7.38 acetyl protons 4.99 $\pi\text{-}C_5H_5$ protons
	1603m	acetyl CO	

[a] In $CHCl_3$ solution. [b] In $CDCl_3$ solution with TMS as internal standard. [c] Data from ref. 3.

The isolation of a triphenylarsineacetylmolybdenum complex suggests that, given appropriate solvent (e.g. acetonitrile) and temperature conditions, other σ-bonded complexes which had not previously undergone CO insertion with As, S and N ligands might be expected to do likewise. Future work will investigate this possibility and also study the decarbonylation of the triphenylarsineacetylmolybdenum complex and any other complex prepared by an analogous procedure to that described above.

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