Journal of Organometallic Chemistry, 99 (1975) C27—C28

Preliminary communication

THE PHOTOCHEMICAL SYNTHESIS OF (π-C_5H_5)Fe($COCH_3$)(CO)E(C_6H_5)$_3$ WHERE E IS ARSENIC OR ANTIMONY

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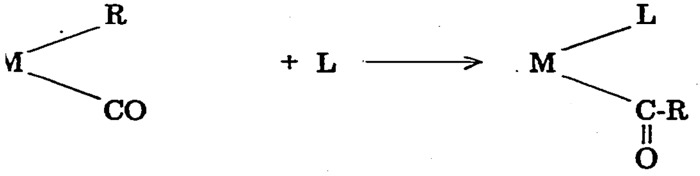
(Received August 19th, 1975)

Summary

UV irradiation of (π-C_5H_5)Fe$(CO)_2CH_3$ in the presence of As$(C_6H_5)_3$ or Sb$(C_6H_5)_3$ in acetonitrile at 20°C gives the title compounds.

Carbon monoxide insertion reactions of the type of eqn. 1 have been



(1)

reported for a large number of σ-bonded ligands (R), metals (represented by M to include ancillary ligands) and incoming nucleophiles (L) [1]. Some transition metal systems react with a wide range of L, including phosphites, phosphines, arsines, stibines, organic sulphides, organic amines, iodide and CO, to yield the corresponding acyls. Other systems, notably (π-C_5H_5)Mo$(CO)_3$R [2] and (π-C_5H_5)Fe$(CO)_2$R [3], display a marked selectively towards various L with phosphorus ligands as the only generally successful type.

We demonstrated recently [4] that As$(C_6H_5)_3$ could react with (π-C_5H_5)Mo$(CO)_3CH_3$ under carefully controlled temperature conditions to give (π-C_5H_5)Mo$(CO)_2$($COCH_3$)As$(C_6H_5)_3$, contrary to what had been reported previously [2]. We report here the conditions under which As$(C_6H_5)_3$ and Sb$(C_6H_5)_3$ react with (π-C_5H_5)Fe$(CO)_2CH_3$ to give new acetyl complexes.

The thermal reaction between (π-C_5H_5)Fe$(CO)_2CH_3$ and excess As$(C_6H_5)_3$ n acetonitrile under N_2, analogous to the successful reaction of (π-C_5H_5)Mo-(CO)$_3CH_3$ [4], was monitored by IR sampling at a range of temperatures

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between 20°C and reflux point. No new IR bands were observed, indicating failure of the thermal route, but on irradiating the reaction mixture with UV/visible light the solution rapidly changed colour, from yellow to deep red. This solution showed the appearance of a single new IR band at 1917 cm^{-1}, which indicated the possible formation of monocarbonyl complex. The reaction on a preparative scale, $(\pi\text{-}C_5H_5)Fe(CO)_2CH_3$ (5 mmole) and $As(C_6H_5)_3$ (20 mmole) in acetonitrile (150 ml) stirred under N_2 at 20°C and irradiated with a 125 watt Hg lamp for 30 minutes through a quartz finger in the centre of the reaction vessel, gave a red-brown solid when the solution was taken to dryness. Repeated washing of the solid with cold methanol removed $As(C_6H_5)_3$ and unreacted $(\pi\text{-}C_5H_5)Fe(CO)_2CH_3$. Recrystallisation of the remaining solid from hexane/methanol gave red-brown crystals of $(\pi\text{-}C_5H_5)Fe(CO)(COCH_3)As(C_6H_5)_3$ (Found: C, 61.30; H, 4.87; N, 0.00. $C_{26}H_{23}AsFeO_2$ calcd.: C, 62.67; H, 4.65; N, 0.00 %) which melted at 127-128°C with an overall yield of 42%. The IR and NMR data (Table 1) are strikingly similar to the corresponding $P(C_6H_5)_3$ complex [3]. An analogous reaction with $Sb(C_6H_5)_3$ gave a dark brown solid which was identified by IR and NMR spectroscopy (Table 1) as $(\pi\text{-}C_5H_5)Fe(CO)(COCH_3)Sb(C_6H_5)_3$. Both new complexes decompose rapidly in many common solvents, e.g. $CHCl_3$, Et_2O, C_6H_6, and this hampered purification.

TABLE 1

IR (2200-1500cm^{-1}) AND NMR (τ) DATA FOR $(\pi\text{-}C_5H_5)Fe(CO)(COCH_3)L$ COMPLEXES

L	IR[a]	NMR[b]
$P(C_6H_5)_3$[c]	1920 vs, terminal CO	7.80, acetyl protons
	1598 s, acetyl CO	5.72, $\pi\text{-}C_5H_5$ protons
		2.45-2.75, phenyl protons
$As(C_6H_5)_3$	1917 vs, terminal CO	8.04, acetyl protons
	1586 m, acetyl CO	5.34, $\pi\text{-}C_5H_5$ protons
		2.55-2.80, phenyl protons
$Sb(C_6H_5)_3$	1916 vs, terminal CO	8.11, acetyl protons
	1582 m, acetyl CO	5.28, $\pi\text{-}C_5H_5$ protons
		2.55-2.75, phenyl protons

[a] In CH_2Cl_2 solution unless stated otherwise. [b] In CS_2 solution with TMS as external standard and using a ^{19}F external lock (Varian XL-100 NMR spectrometer). [c] IR data from ref. 3; in $CHCl_3$ solution.

The isolation of triphenylarsine- and triphenylstibine-acetyliron complexes suggests that other σ-bonded complexes, which had not previously undergone thermal CO insertion reactions with As, N and S ligands, might react successfully under UV/visible irradiation. Future work will investigate this possibility and also study the decarbonylation of the new complexes.

References

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