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NOTE

SOME ALKYNYL DERIVATIVES OF IRON AND MOLYBDENUM

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In the course of a study of simple organic systems σ-bonded to transition metals, we have prepared alkynyl derivatives of some mixed carbonyl-π-cyclopentadienyl transition metal complexes. Treatment of the metal halides, π-$C_5H_5Fe(CO)_2Cl$ or π-$C_5H_5Mo(CO)_3Cl$, with tetrahydrofuran solutions of $RC{\equiv}CMgBr$ (R = n-butyl, phenyl) gave good yields of the corresponding alkynyl compounds, π-$C_5H_5Fe(CO)_2$-$C{\equiv}CR$ or π-$C_5H_5Mo(CO)_3C{\equiv}CR$.

The four complexes so prepared were stable in air for prolonged periods (many months in the case of π-$C_5H_5Fe(CO)_2C{\equiv}CPh$), and decomposed only slowly in chloroform. Exhaustive attempts to hydrogenate π-$C_5H_5Fe(CO)_2C{\equiv}CPh$ failed, even when Adam's catalyst was used. This compound was decomposed by concentrated aqueous hydrochloric acid or by hydrogen chloride in organic solvents, but not by dilute aqueous acid, and the parent chloride, π-$C_5H_5Fe(CO)_2Cl$ was isolated as a product.

Gas was evolved upon treatment of π-$C_5H_5Fe(CO)_2C{\equiv}CPh$ with triphenylphosphine at 160°, and π-$C_5H_5FeCO(PPh_3)C{\equiv}CPh$ was then crystallised from benzene/light petroleum in good yield. π-$C_5H_5FeCO(PPh_3)C{\equiv}CC_4H_9$ was prepared similarly. There was no evidence in these reactions of the insertion of carbon monoxide into the carbon–metal bond to give an acylmetallic compound; by contrast the corresponding alkyliron compounds do yield acyl compounds on treatment with triphenylphosphine[1].

Infrared and analytical data for the alkylmetallic compounds, given in Table 1, and proton magnetic resonance spectral data, given below, are consistent with the proposed structures. The observed coupling ($J = 1.1$ cps) between the π-cyclopentadienyl protons and the phosphorus nucleus in π-$C_5H_5FeCO(PPh_3)C{\equiv}CPh$ is worthy of note. The mass spectrum of π-$C_5H_5Fe(CO)_2C{\equiv}CPh$ showed the parent ion ($m/e = 278$) and fragments including $FeC{\equiv}CPh^+$ ($m/e = 157$). The most prominent metastable peak ($m/e = 124$) corresponds to the reaction π-$C_5H_5FeC{\equiv}CPh^+ \rightarrow \pi$-$C_5H_5$-$C{\equiv}CPh^+ + Fe$.

The extent of π-bonding between alkynyl groups and transition metals is unknown. The observation of a lower $C{\equiv}C$ stretching frequency for the triphenylphos-

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TABLE 1

ALKYNYL DERIVATIVES OF IRON AND MOLYBDENUM PREPARED

Compound	Colour and m.p. (°C)	$\nu(C\equiv C)$	$\nu(C\equiv O)$	Analysis: found (calcd.) (%)		
				C	H	Fe
π-$C_5H_5Fe(CO)_2C\equiv CPh$	Yellow	2105m	2000s	64.4	3.6	19.9
	120–122 (dec.)		2045m	(64.3)	(3.5)	(20.1)
π-$C_5H_5Fe(CO)_2C\equiv CC_4H_9$	Yellow	2125w	1930s	60.5	5.4	21.3
	liq.		2045s	(60.5)	(5.4)	(21.7)
π-$C_5H_5FeCO(PPh_3)C\equiv CPh$	Brown	2085w	1950s	74.7	4.9	11.1
	194–196 (dec.)			(75.0)	(4.9)	(10.9)
π-$C_5H_5FeCO(PPh_3)C\equiv CC_4H_9$	Brown	2095w	1945s	72.2	4.8	
	129–132			(73.2)	(5.9)	
π-$C_5H_5Mo(CO)_3C\equiv CPh$	Yellow-green	2100w	1960s	55.7	2.9	
	55 (dec.)		1970s	(55.5)	(2.9)	
			2045s			
π-$C_5H_5Mo(CO)_3C\equiv CC_4H_9$	Yellow-green	2100w	1960s	51.4	4.4	
	126 (dec.)		1970s	(51.3)	(4.3)	
			2045s			

phine compounds of iron than for the parent dicarbonyls, suggestst that π-bonding does occur.

EXPERIMENTAL

(*Phenylethynyl*)-π-*cyclopentadienyliron dicarbonyl*

Butylmagnesium bromide was prepared by addition of butyl bromide (2.74 g, 20 mmole) and tetrahydrofuran (10 ml) to magnesium turnings (1.0 g) under nitrogen. When reaction was complete, phenylacetylene (2.5 ml, *i.e.* excess) was added and the mixture was warmed to 40° for 30 min to complete the evolution of butane. The Grignard reagent was then diluted with further tetrahydrofuran (20 ml), and the supernatant solution was siphoned slowly under nitrogen into a stirred solution of π-cyclopentadienyliron dicarbonyl chloride (2.4 g, 12 mmole) in tetrahydrofuran (20 ml) at $-60°$ under nitrogen. The resulting solution was allowed to warm to room temperature, and was then hydrolysed by pouring into dilute (1:20) aqueous hydrochloric acid. The oil which separated slowly solidified, and was then filtered, dissolved in ether, and precipitated by addition of light petroleum to give π-$C_5H_5Fe(CO)_2$-$C\equiv CPh$ (2.0 g, 60% yield) as a yellow solid, m.p. 120–122° (dec.), which could be recrystallised from ethanol and sublimed.

The other alkynylmetallic compounds were prepared similarly but in lower yields; in these cases hydrolysis was followed by chromatography on aluminium.

Proton magnetic resonance spectra

Spectra were determined in deuterochloroform using a Perkin–Elmer 60 Mc spectrometer. Chemical shifts (ppm) are given on the τ scale.

π-$C_5H_5Fe(CO)_2C{\equiv}CPh$	2.7 (complex)[a];	4.95 (singlet)[b]
π-$C_5H_5FeCO(PPh_3)C{\equiv}CPh$	2–3 (complex)[a];	5.43 [doublet $J(P\text{–}H) = 1.1$ cps][b]
π-$C_5H_5Fe(CO)_2C{\equiv}CC_4H_9$	5.00 (singlet)[b]	7.6–9.3 (three multiplets)[c]
π-$C_5H_5Mo(CO)_3C{\equiv}CPh$	2.6–3.8 (complex)[a];	4.43 (singlet)[b]
π-$C_5H_5Mo(CO)_3C{\equiv}CC_4H_9$	4.51 (singlet)[b];	7.66–9.25 (three multiplets)[c]

[a] Phenyl protons. [b] π-C_5H_5 protons. [c] C_4H_9 protons.

Mass spectra

A Hitachi Perkin–Elmer instrument operating at an ionising voltage of 70 e.v. was used.

REFERENCE

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