778. *Some Transition-metal Propionyl Complexes and a Novel Ethyl Transfer Reaction.*

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Some propionyl complexes of transitional metals have been prepared and the infrared and nuclear magnetic resonance spectra determined. During the preparation of the tricarbonyl-π-cyclopentadienylpropionylmolybdenum compound, by carbon monoxide insertion into the corresponding ethyl compound, it was found that on heating the latter the ethyl group is transferred to the cyclopentadienyl ring giving the corresponding binuclear carbonyl species and other products typical of a free-radical reaction.

During studies of some transition-metal ethyl complexes of the type $\pi\text{-}C_5H_5M(CO)_nC_2H_5$,[1] it was found necessary to prepare analogous compounds in which a carbonyl group was inserted between the transition metal and the ethyl radical. Proton magnetic resonance

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[1] Davison, McCleverty, and Wilkinson, *J.*, **1963**, 1133.

studies showed that such propionyl complexes have " normal " ethyl groups (τ_{CH_2} *ca.* 7—8, τ_{CH_3} *ca.* 9) in contrast to the case where the ethyl group is bound directly to the metal, *e.g.*, π-$C_5H_5Mo(CO)_3C_2H_5$ (τ_{CH_2} 8·34, τ_{CH_3} 8·52).

Of the four propionyls prepared, π-$C_5H_5M(CO)_2CO{\cdot}C_2H_5$ (M = Fe, Ru) and π-$C_5H_5M(CO)_3CO{\cdot}C_2H_5$ (M = Mo, W), the molybdenum species proved to be the most unstable and difficult to purify. The iron, ruthenium, and tungsten derivatives were prepared by treating the sodium salts, π-$C_5H_5M(CO)_nNa$, in dry tetrahydrofuran with propionyl chloride.[2] Although this method was used in an attempt to prepare the molybdenum propionyl, only traces were found (by nuclear magnetic resonance techniques) and the complex was eventually prepared by insertion of carbon monoxide under pressure.[3]

The product of the reaction between π-$C_5H_5Mo(CO)_3C_2H_5$ and carbon monoxide at 100 atm. and at 80° or 100° was shown to contain two products both having " normal " ethyl groups (see Table). It seemed possible that at temperatures above the melting point of the ethyl compound (77·5—78·5°) the C_2H_5 group could migrate from the transition metal to the cyclopentadienyl ring giving a binuclear molybdenum complex $\{(\pi\text{-}C_5H_4{\cdot}C_2H_5)Mo(CO)_3\}_2$. That the ethyl group is transferred above the melting point (in the absence of carbon monoxide) was demonstrated by heating pure π-$C_5H_5Mo(CO)_3C_2H_5$ for 2 hr. at 100° in a sealed evacuated tube. On cooling, red crystals were formed which were chromatographed on alumina columns. Although the first and the second band were eluted from the chromatography columns together and could not be cleanly separated by further chromatography, the main product isolated was $\{(\pi\text{-}C_5H_4C_2H_5)Mo(CO)_3\}_2$. The second unidentified species may have been a monoethyl derivative $\{(\pi\text{-}C_5H_4{\cdot}C_2H_5)Mo(CO)_6Mo(\pi\text{-}C_5H_5)\}$. The third species was the unsubstituted complex $\{\pi\text{-}C_5H_5Mo(CO)_3\}_2$.

Spectroscopic data for propionyl complexes.

Compound	τ_{cp}	τ_{CH_2}	τ_{CH_3}	Carbonyl stretching frequencies (cm.$^{-1}$)
π-$C_5H_5Fe(CO)_2CO{\cdot}C_2H_5$ ...	5·56 *	7·28	9·16	2026s, 1960s, 1840vw, 1759vw, 1657s §
π-$C_5H_5Ru(CO)_2CO{\cdot}C_2H_5$ ...	4·69 †	7·80	8·99	2032s, 1960s, 1850vw, 1710vw, 1630m §
π-$C_5H_5Mo(CO)_3CO{\cdot}C_2H_5$ ...	5·41 *	7·82	8·98	2016s, 1930s, 1708w, 1675s §
π-$C_5H_5W(CO)_3CO{\cdot}C_2H_5$	4·40 ‡	7·12	9·18	2014s, 1932s, 1740w, 1640m §
$[\pi\text{-}(C_5H_4C_2H_5)Mo(CO)_3]_2$ ...	4·68 ‡	7·08	8·81	2015m, 1960s, 1910s

* In benzene. † In dichloromethane. ‡ In carbon tetrachloride. § Ketonic carbonyl stretching frequency.

Evidence for the formation of the first species is as follows. Proton magnetic resonance studies show that it has a " normal " ethyl group (see Table) and the infrared spectrum shows the expected aliphatic C–H stretching frequencies in the range 2800—3000 cm.$^{-1}$. Only two CO stretching frequencies are observed which correspond to those observed in similar ring-substituted complexes.[4] The ultraviolet absorption spectrum in benzene shows $\lambda_{max.}$ 510 (ε 1415) and 390 mμ (ε 12,680), again comparable with those for similar complexes.

It had already been noted [5] that transition-metal alkyls of the type under discussion decompose to red solids when heated or left in sunlight, although the products were not investigated at the time. A number of other similar complex carbonyl methyl and ethyl compounds have now been exposed to ultraviolet radiation, but only the above molybdenum ethyl complex showed any tendency to form the ring-substituted product. All the other complexes, particularly the tungsten ones, gave unsubstituted binuclear species.

The decomposition of π-$C_5H_5Mo(CO)_3C_2H_5$ is accompanied by the formation of condensable gaseous hydrocarbons (98%) and a non-condensable gas (2%). The condensable hydrocarbons were identified by gas–liquid chromatography as ethylene and/or

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[2] Closson, Kozikowski, and Coffield, *J. Org. Chem.*, 1957, **22**, 598.

[3] Closson, Coffield, and Kozikowski, Internat. Conference on Co-ordination Chemistry, London, 1959, *Chem. Soc. Special Publ.* No. 13, p. 126.

[4] Abel, Singh, and Wilkinson, *J.*, 1960, 1321.

[5] Piper and Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **3**, 104.

ethane, n-butane, and two C_5 fractions (ratio *ca.* 1 : 50; b. p. 36° ± 2° and 42° ± 2°). The overall ratios were *ca.* 1 : 8 : 1 : 800; the C_5 species may have been diethyl ether and either a branched pentene, penta-2,3-diene, cyclopentadiene, or cyclopentane. The non-condensable gas contained *ca.* 99% of methane and *ca.* 1% of hydrogen. The infrared spectrum of the gas showed no peaks in the region 2000—2200 cm.$^{-1}$, indicating that carbon monoxide was not released during the decomposition.

A radical mechanism may be postulated in which homolysis of the ethyl-molybdenum bond occurs easily in the melt, allowing the ethyl radical either to dimerise (forming n-C_4H_{10}) or to attack the π-C_5H_5 ring forming (π-$C_5H_4{\cdot}C_2H_5$)Mo(CO)$_3{\cdot}$ and H$\cdot$; the larger radical then dimerises. It might be expected that, if this mechanism were feasible, the main products of the decomposition would be n-butane and the unsubstituted binuclear molybdenum complex. Butane is observed in the reaction gases, as well as lower and higher-boiling hydrocarbons; the formation of these in a radical decomposition is not surprising. Further, the ethyl complex was never obtained in yields greater than 10% (based on the starting material), the unsubstituted species being the main binuclear complex isolated. Also, no substitution on the ring was expected or found when the decomposition was carried out in light petroleum (b. p. 80—100°).

Experimental.—Microanalyses were by the Microanalytical Laboratory of this College. High-resolution proton magnetic resonance spectra were measured on a Varian Associates spectrometer V4311 at 56·46 Mc./sec. at 22° ± 2°. Line positions were measured by conventional side-band techniques. Infrared spectra were taken on a Perkin-Elmer model 21 spectrophotometer with sodium chloride optics. Ultraviolet absorption spectra were recorded on a Perkin-Elmer Spectracord 4000 instrument, with degassed benzene and silica cells.

Dicarbonyl-π-cyclopentadienylpropionyliron. Tetracarbonyldi-π-cyclopentadienyldi-iron (5 g.) was stirred vigorously for 15 min. with an excess of 1% sodium amalgam in tetrahydrofuran (50 ml.). The amalgam was separated and the solution containing the sodium salt was dripped slowly at room temperature into a solution of propionyl chloride (8 ml.) in tetrahydrofuran (50 ml.) under nitrogen. The mixture was stirred for 1 hr. and the solvent then removed *in vacuo*. The residue was extracted with light petroleum (b. p. 40—60°; 2 × 30 ml.), and the extract filtered. The petroleum was evaporated at 40°/0·1 mm., leaving an orange-red oil. Chromatography of this oil on alumina (Spence's grade 3) in light petroleum (b. p. 40—60)–benzene indicated that no further purification was necessary after extraction from the residue. The *compound* is stable in air, very slightly volatile, and soluble in common organic solvents (Found: C, 51·5; H, 4·6; O, 20·6. $C_{10}H_{10}O_3Fe$ requires C, 51·3; H, 4·6; O, 20·5%).

Dicarbonyl-π-cyclopentadienylpropionylruthenium and *tricarbonyl-π-cyclopentadienylpropionyltungsten* were prepared in the same way. The former is a pale yellow oil, stable in air (Found: C, 43·3; H, 3·8; O, 17·4. $C_{10}H_{10}O_3Ru$ requires C, 43·2, H, 3·9; O, 17·3%). The latter is a waxy orange solid, m. p. *ca.* 5° (Found: C, 33·6; H, 2·6; O, 16·4. $C_{11}H_{10}O_4W$ requires C, 33·8; H, 2·6; O, 16·4%).

Tricarbonyl-π-cyclopentadienylpropionylmolybdenum. Tricarbonyl-π-cyclopentadienylethylmolybdenum (5 g.) was treated with carbon monoxide (100 atm.) for 3 hr. at room temperature. The red oil which was formed was extracted with light petroleum (b. p. 40—60°; 2 × 60 ml.) and the solution filtered and evaporated at 40°/0·1 mm. The residual red oil was shown, by its proton magnetic resonance spectrum in benzene and by its infrared spectrum in carbon disulphide, to contain π-$C_5H_5Mo(CO)_3CO{\cdot}C_2H_5$. Further purification by chromatography or by re-extraction into light petroleum was very difficult as the compound is very sensitive to oxygen and is thermally unstable, decomposing to give $\{\pi\text{-}C_5H_5Mo(CO)_3\}_2$ and other unidentified products.

Hexacarbonyldi-π-ethylcyclopentadienyldimolybdenum. Tricarbonyl-π-cyclopentadienylethylmolybdenum was heated at 100° in a sealed evacuated Carius tube for 3 hr. A red oil was formed which crystallised on cooling. The tube was opened and the contents washed with light petroleum (b. p. 30—40°). The remaining red crystals were dissolved in benzene and chromatographed under nitrogen on alumina (Spence's grade 3) in light petroleum–benzene (40 : 60). Three bands separated, the first two bands being eluted together. The solvent was evaporated, leaving a dark red solid. Further chromatography of this solid in light petroleum–benzene gave no separation. The red solid was identified as $\{(\pi\text{-}C_5H_4C_2H_5)Mo(CO)_3\}_2$, m. p. 210—211°, soluble in chloroform, carbon disulphide, carbon tetrachloride, and benzene (Found: C, 43·8; H, 3·1; O, 17·8. $C_{20}H_{18}O_3Mo_2$ requires C, 44·0; H, 3·3; O, 17·6%).

Gas analysis. The gas from thermal decomposition of $\pi\text{-}C_5H_5Mo(CO)_3C_2H_5$ (*ca.* 2 g.) was collected and analysed chromatographically on three columns. The first sample was injected on to a silica-gel column (length 7 ft., packed with 28—60 mesh Davison silica gel kept at constant temperature by an acetone-vapour jacket). A katharometer detector was used with oxygen-free nitrogen as the carrier gas. Hydrogen and methane were detected; carbon monoxide and dioxide, acetylene, ethylene, and ethane were absent. The second sample was injected on to a silicone-oil column (length 7 ft., the oil supported in 40—60 May and Baker Embacel maintained at constant temperature by an acetone-vapour jacket). Again, a katharometer detector was employed, oxygen-free nitrogen acting as the carrier gas. Methane, ethylene and/or ethane, and n-butane were identified; other C_2, C_3, C_4, C_5, and C_6 hydrocarbons were absent. In order to detect the presence of low-boiling oxygenated hydrocarbons, the third sample was injected on to a 20% polyethyleneglycol column [length 15 ft., with polyethylene glycol (PEG 400) supported on 40—60 Embacel (washed with alcoholic potassium hydroxide), maintained at constant temperature by an acetone-vapour jacket). A thermocouple detector was used with hydrogen (75%) and nitrogen (25%) as carrier gas. Traces of methane and C_2 hydrocarbons were observed as well as n-butane. Two fractions were observed in the C_5 region, the smaller being probably ether impurity and the larger either a branched pentene, penta-2,3-diene, cyclopentadiene, or cyclopentene. The b. p.s of the two C_5 species were 36° ± 2° and 42° ± 2°, respectively.

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