Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

SOME σ-PHENACYL COMPLEXES OF TRANSITION METALS

M. ISHAQ
Brandeis University Department of Chemistry, Waltham, Mass. (U.S.A.)

(Received November 29th, 1967)

There has been considerable interest in recent years in the preparation of σ-bonded complexes of transition metals. Here we report the synthesis and characterization of σ-bonded phenacyl complexes of Mo and Fe. The complexes were prepared in tetrahydrofuran by the reaction of the corresponding complexed transition metal anions, π-$C_5H_5Mo(CO)_3^-$ and π-$C_5H_5Fe(CO)_2^-$ with α-chloroacetophenone (phenacyl chloride).

Both complexes are yellow solids, soluble in common organic solvents. The iron compound, π-$C_5H_5Fe(CO)_2$–$CH_2COC_6H_5$, is more stable in air than the corresponding molybdenum analog, but nevertheless it decomposes to the extent of 50% in air in two days.

TABLE 1

INFRARED SPECTRA, MELTING POINTS AND COLORS

Compound	Metal–carbonyl freq. (cm^{-1})	Keto freq. (cm^{-1})	M.p. (°C)	Color
π-$C_5H_5Mo(CO)_3$–$CH_2COC_6H_5$	2021vs, 1948vs[a], 1918vs	1615vs	85–86	Orange-yellow
π-$C_5H_5Fe(CO)_2$–$CH_2COC_6H_5$	2011vs, 1950vs[b]	1625vs	91–92	Yellow

[a] The infrared spectrum (KBr pellet) shows a shoulder at 1895 cm^{-1}. [b] The infrared spectrum (KBr pellet) shows shoulders at 1929 and 1921 cm^{-1}.

The complexes are characterized by their infrared spectra (see Table 1 and *Experimental* section), proton magnetic resonance spectra (see Table 2) and elemental analyses (see *Experimental* section). The proton magnetic resonance spectra of π-$C_5H_5Mo(CO)_3$–$CH_2COC_6H_5$ and π-$C_5H_5Fe(CO)_2$–$CH_2COC_6H_5$ show sharp singlets corresponding to the π-C_5H_5 and methylene protons, showing that the complexes are diamagnetic. The splitting of the protons of the phenyl group is analogous to that of acetophenone[1] and may be assigned similarly; that is, the 2,6-protons are observed at lower field than the 3,4,5-protons which occur at higher field (see Fig. 1 and Table 2 for assignments).

TABLE 2

PROTON MAGNETIC RESONANCE SPECTRA

Compound	τ (ppm)[a]	Relative intensity	Multiplicity	Assignment
π-$C_5H_5Mo(CO)_3$-$CH_2COC_6H_5$ in $CDCl_3$	2.18 centre	2	Multiplet	2,6-protons of C_6H_5
	2.57 centre	3	Multiplet	3,4,5-protons of C_6H_5
	4.65	5	1	π-C_5H_5
	7.37	2	1	Mo-CH_2
π-$C_5H_5Fe(CO)_2$-$CH_2COC_6H_5$ in $CDCl_3$	2.2 centre	2	Multiplet	2,6-protons of C_6H_5
	2.57 centre	3	Multiplet	3,4,5-protons of C_6H_5
	5.24	5	1	π-C_5H_5
	7.69	2	1	Fe-CH_2

[a] Relative to Me_4Si (τ 10) as an internal reference.

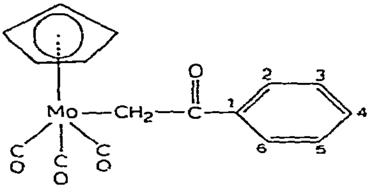

Fig. 1

EXPERIMENTAL

All the reactions were carried out under an atmosphere of nitrogen or in vacuum. The THF was dried over $LiAlH_4$. The microanalyses were carried out by Schwarzkopf Microanalytical Laboratory, N.Y. The infrared spectra were recorded as KBr pellets using Perkin Elmer Model 257 Grating Infrared Spectrophotometer. Proton magnetic resonance spectra were determined on a Varian Associate NMR Instrument at 60 Mcps.

Tricarbonyl-σ-phenacyl-π-cyclopentadienylmolybdenum

A solution of sodium salt $Na^+[\pi\text{-}C_5H_5Mo(CO)_3]^-$ (4.0 g) in tetrahydrofuran (20 ml) was prepared as described elsewhere[2]. This solution was slowly transferred to a stirred and cooled (−30°) (dry ice/acetone bath) solution of α-chloroacetophenone (2.5 g) in tetrahydrofuran (5 ml). After addition (20 min) the reaction mixture was allowed to warm to room temperature and was stirred for another 1 h. The solvent was removed under reduced pressure. The reaction product was extracted with petroleum ether and chromatographed on an alumina column made in ether. Elution with petroleum ether/ether mixture (50:50) separated first a red band which was collected and identified by its infrared spectrum as the binuclear complex $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ and secondly a yellow band. This band was eluted with ether. The solvent was removed under reduced pressure and the yellow solid was recrystallized from ether/pentane mixture giving orange yellow crystals of $\pi\text{-}C_5H_5Mo(CO)_3CH_2COC_6H_5$. Yield ~30%. The infrared spectrum shows bands at 3107w, 2998vw, 2941w, 1591w, 1571w, 1444w, 1428m, 1418m, 1310w, 1295w, 1268vs, 1175w, 1119w, 1079vw, 1029w, 1015m, 1005m, 940vw, 929vw, 848w, 825m, 798m, 711 s cm^{-1}. For keto and metal–carbonyl stretching frequencies see Table 1. (Found: C, 52.8; H, 3.5. $C_{16}H_{12}MoO_4$, calcd.: C, 52.7; H, 3.3%.)

Dicarbonyl-σ-phenacyl-π-cyclopentadienyliron

Sodium dicarbonylcyclopentadienyliron (2.0 g) was prepared from binuclear complex $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ in tetrahydrofuran as described previously[2]. This was treated with α-chloroacetophenone (1.5 g) as described above in the preparation of molybdenum analog. The reaction product was extracted with petroleum ether/ether mixture (5:1) and chromatographed on an alumina column made in ether. Elution with petroleum ether/ether (50:50) mixture separated first a red band which was collected and identified by its infrared spectrum as binuclear compound $[\pi\text{-}C_5H_5Fe(CO)_2]_2$. The second yellow band was eluted with ether. The solvent was removed under reduced pressure and the yellow solid was crystallized twice from 30–40° petroleum ether giving yellow crystals of $\pi\text{-}C_5H_5Fe(CO)_2\text{–}CH_2COC_6H_5$. Yield ~20%. The infrared spectrum shows bands at 3096w, 3080m, 3000w, 2954w, 1594w, 1571m, 1448m, 1428m, 1419m, 1357w, 1308m, 1300vw, 1270vs, 1177w, 1157w, 1112m, 1078vw, 1065w, 1034w, 1018s, 1004w, 938w, 882vw, 850s, 805m, 782w, 728m, 708s, 688w cm^{-1}. See Table 1 for keto and metal–carbonyl stretching frequencies. (Found: C, 60.3; H, 4.4. $C_{15}H_{12}FeO_3$, calcd.: C, 60.8; H, 4.0%.)

ACKNOWLEDGEMENT

I wish to thank Prof. M. Rosenblum for his helpful suggestions in preparing this manuscript.

REFERENCES

1 *Varian High Resolution NMR Spectra Catalogue.*
2 T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 3 (1956) 104.