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

Preliminary communication

Preparation of (h^5-cyclopentadienyl)(t-butyl)iron dicarbonyl

WARREN P. GIERING and M. ROSENBLUM
Edison-Lecks Laboratories, Department of Chemistry, Brandeis University, Waltham, Mass. 02154 (U.S.A.)

(Received July 6th, 1970; by publisher October 5th, 1970)

Of the several methods by which complexes containing transition metal—carbon σ-bonds may be prepared, the reduction of metal—olefin cation complexes with borohydride has remained comparatively obscure, a circumstance owing no doubt to the apparent lack of generality of the method[*]. A limited number of such cation complexes of iron[1], molybdenum[2] and tungsten[3], which were prepared either by protonation of h^1-allyl complexes[2–4] or by hydride abstraction from alkyl complexes[1], have been converted to alkyl derivatives in this manner.

We have now found that the method is applicable to the synthesis of (h^5-cyclopentadienyl)(t-butyl)iron dicarbonyl. This substance represents the first transition metal complex containing a t-butyl—transition metal bond, and is remarkable for its thermal and chemical stability[**].

(h^5-Cyclopentadienyl)(i-butenyl)iron dicarbonyl (I) was prepared from sodium(h^5-cyclopentadienyl)dicarbonyl ferrate and methallyl chloride in 86% yield. Treatment of this substance with 48% aqueous hydrofluoroboric acid in acetic anhydride gave the tetrafluoroborate salt (IIa) as a yellow crystalline material. (*Anal.*: Found: Fe, 17.50[***]. $C_{11}H_{13}FeO_2BF_4$ calcd.: Fe, 17.50%). This substance (8.5 g, 26.5 mmoles) was reduced with sodium borohydride in tetrahydrofuran to give a 3/1 mixture of t-butyl and i-butyl complexes (IIIa and IVa) as a viscous orange oil. The formation of the isomeric products (IIIa and IVa) resulting from hydride addition to both the primary and tertiary carbon centers is noteworthy since similar reduction of the propylene complex (IIb) is reported to give only the i-propyl derivative (IIIb)[1].

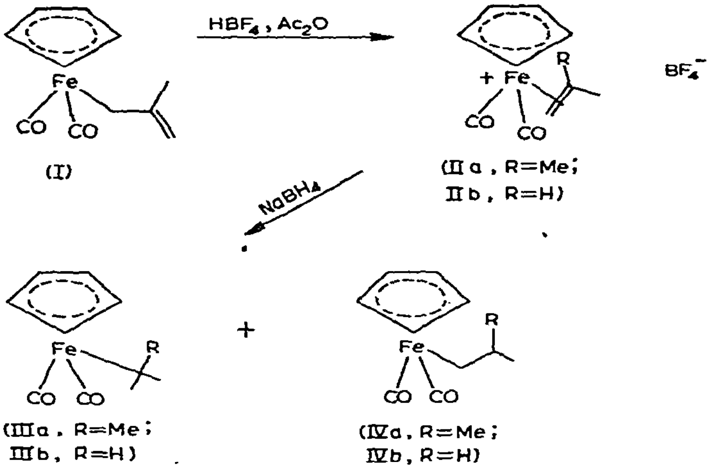
Purification of the reaction mixture was achieved by taking advantage of the very great difference in chemical reactivity of the isomeric alkyl complexes. Thus, treatment of

---

[*] A general review of the methods used to prepare σ-alkyl and σ-aryl derivatives of transition metals has recently been provided by Parshall and Mrowca[6], but no mention is made of this method among those enumerated.

[**] An earlier attempt to prepare this substance by the reaction of sodium (h^5-cyclopentadienyl)dicarbonyl ferrate with t-butyl chloride gave (h^5-cyclopentadienyl)iron dicarbonyl dimer, (h^5-cyclopentadienyl)iron dicarbonyl hydride and isobutylene[1].

[***] Iron analyses were carried out on a Perkin—Elmer model 305 atomic absorption spectrophotometer.



the reaction product above with gaseous hydrogen chloride (4.5 mmoles, 200 mm, 25°) for 15 h resulted in selective destruction of the isobutyl derivative. The resulting mixture was purified by chromatography on alumina and gave the t-butyl complex (IIIa) in 24% yield (based on IIa) as orange-yellow crystals, m.p. 72–75°. (*Anal.*: Found: C, 56.43; H, 6.27; Fe, 24.6. $C_{11}H_{14}FeO_2$ calcd.: C, 56.48; H, 5.97; Fe, 23.9%.) The substance is air stable for brief periods, and may be sublimed unchanged at 25° under high vacuum. It decomposes slowly at room temperature over a period of several days to give isobutylene as the principal condensable gaseous product. Prolonged treatment of (IIIa) with gaseous hydrogen chloride gives, as expected, i-butane and (h^5-cyclopentadienyl)iron dicarbonyl chloride in addition to carbon monoxide and other unidentified decomposition products.

In accord with its structure, the NMR spectrum of IIIa exhibits only two singlet proton signals at δ 4.65 and 1.30 (CS_2 solution) with relative integrated areas of 5 and 9, assignable to cyclopentadienyl and methyl protons respectively.

The mass spectrum of IIIa exhibits a weak ion current for the parent molecule ion at *m/e* 234, and comparatively intense peaks at *m/e* 178 ($CpFeC_4H_9$), 176 ($CpFeC_4H_7$), 150 ($CpFeC_2H_5$), 122 (CpFeH), 121 (CpFe) and 56 (Fe), a fragmentation pattern largely paralleling that of other $CpFe(CO)_2R$ complexes (R = ethyl, n-propyl, i-butyl, neopentyl). In contrast to these, however, the spectrum of IIIa exhibits a strong peak for R^+ at *m/e* 57 reflecting the increased stability of the tertiary cation.

The infrared spectrum of (IIIa) exhibits carbonyl absorption at 2002 and 1946 cm^{-1}. A comparison of the absorption of the substance with the corresponding absorptions of a series of iron-alkyl derivatives, summarized in Table 1, reveals a progressive decrease in carbonyl frequency as hydrogen is successively replaced by a methyl group, suggestive of a concomitant increase in the electron donor power of the alkyl group.

The present results suggest that previous failure to prepare transition metal complexes containing a t-alkyl–metal bond[5] may be less a consequence of the inherent thermodynamic or kinetic instability of such substances than of the methods chosen to synthesize them.

The preparation of other t-butyl–metal complexes by hydride reduction of olefin–metal complex cations is being examined.

TABLE 1

CARBONYL ABSORPTION FREQUENCIES FOR h^5-CpFe$(CO)_2$R [a]

R	ν_1	ν_2
CH_3	2012	1959
CH_2CH_3	2008	1954
$CH(CH_3)_2$	2006	1952
$C(CH_3)_3$	2002	1946

[a] Infrared spectra were obtained in n-hexane solutions (1 mg/ml) using a Perkin–Elmer model 521 grating infrared spectrophotometer. All spectra were calibrated by comparison with the vibrational-rotational spectrum of DCl (I.U.P.A.C. Tables For The Calibration of Infrared Spectrometers, Butterworth, London). Spectra were reproducible to within 0.3 cm^{-1}.

ACKNOWLEDGEMENT

Financial support of this research by the National Institutes of Health (GM-16395) and by the National Science Foundation (GP-8714) is gratefully acknowledged.

REFERENCES

1 M.L.H. Green and P.L.I. Nagy, *J. Organometal. Chem.*, 1 (1963) 58.
2 M. Cousins and M.L.H. Green, *J. Chem. Soc.*, (1963) 889.
3 M.L.H. Green and A.N. Stear, *J. Organometal. Chem.*, 1 (1964) 230.
4 M.L.H. Green and P.L.I. Nagy, *J. Chem. Soc.*, (1963) 189.
5 R.B. King, *Advan. Organometal. Chem.*, 2 (1964) 207.
6 G.W. Parshall and J.J. Mrowca, *Advan. Organometal. Chem.*, 7 (1968) 157.