Preliminary communication

REVERSAL OF THE BONDING MODE OF μ-C$_7$H$_7$ ON AN Fe—Rh FRAMEWORK: SYNTHESIS AND STRUCTURE OF (μ-C$_7$H$_7$)(μ-CO)Fe(CO)$_2$Rh(dppe)*

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Summary

Phosphine ligands rapidly displace one or two carbonyl groups from (μ-C$_7$H$_7$)-Fe(CO)$_3$Rh(CO)$_2$ (I). The substitution occurs exclusively at the Rh center and proceeds with reversal of the bonding mode of the μ-C$_7$H$_7$ moiety from η^4-Rh and η^3-Fe in I to η^3-Rh and η^4-Fe in (μ-C$_7$H$_7$)(μ-CO)Fe(CO)$_2$Rh(dppe).

Coordinative unsaturation is of paramount importance for reactions, stoichiometric or catalytic, to occur at transition metal centers [1]. This unsaturation can be brought about by a variety of means but a particularly interesting class of compounds are those containing polyhapto bound organic ligands where hapticity changes can in principle produce the requisite electron deficient reactive intermediates [2]**. An interesting recent example is the report by Casey et al. [3] on the conversion of η^5-C$_5$H$_5$ to η^1-C$_5$H$_5$ bonding mode by PMe$_3$. Kinetic investigation by Casey [3] for the above conversion and, as early as 1965, by Basolo et al. [3] on the substitution of CO by PPh$_3$ on (η^5-C$_5$H$_5$)Rh(CO)$_2$, established the associative nature of these reactions and argued eloquently for the intermediacy of a slipped η^3-C$_5$H$_5$ moiety. By virtue of its known variable bonding capability*** the C$_7$H$_7$ moiety should be an excellent candidate in this regard also. Here we present preliminary results which confirm this hypothesis.
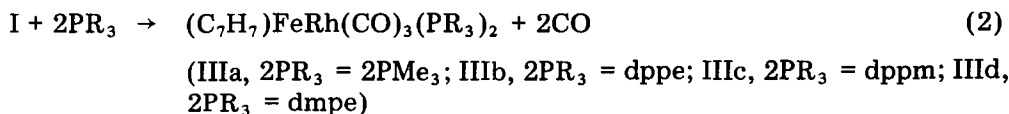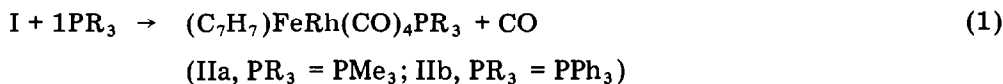
In the initial report on the synthesis of (μ-C$_7$H$_7$)Fe(CO)$_3$Rh(CO)$_2$ (I) [5], it was noted that the molecule exchanges ^{13}CO very readily. To pinpoint the initial site of attack, the reaction of I toward phosphines was investigated.

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*Abbreviations: Ph = C$_6$H$_5$, Me = CH$_3$, dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$, dppm = Ph$_2$PCH$_2$PPh$_2$, dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$.

**We suggest the designation "incipient coordinative unsaturation" for these formally saturated organometallic species.

***Examples of η^1-, η^3-, η^5- and η^7-C$_7$H$_7$ moieties have been reported.

I reacts readily with a variety of phosphines to give mono- and di-substituted complexes depending on the reaction stoichiometry (eq. 1 and eq. 2). The ^{31}P NMR spectrum of the molecules, II and III, shows only one doublet

$$I + 1PR_3 \rightarrow (C_7H_7)FeRh(CO)_4PR_3 + CO \tag{1}$$

$$(IIa, PR_3 = PMe_3; IIb, PR_3 = PPh_3)$$

$$I + 2PR_3 \rightarrow (C_7H_7)FeRh(CO)_3(PR_3)_2 + 2CO \tag{2}$$

(IIIa, $2PR_3 = 2PMe_3$; IIIb, $2PR_3 = $ dppe; IIIc, $2PR_3 = $ dppm; IIId, $2PR_3 = $ dmpe)

$(J(^{103}Rh-^{31}P) \approx 170$ Hz), clearly establishing the location of the PR_3 ligand(s) on the rhodium atom*. It is interesting that the second PR_3 molecule, even in the case of dppm which is prone to produce bridged dimetal species, attacks rhodium as well to give the symmetrical compound III**. Undoubtedly the propensity of Rh to form 16-electron complexes in preference to Fe is the reason behind this observation.

The infrared spectra of the complexes II and III revealed the presence of both terminal and bridging carbonyl moieties. In particular the simple three band spectrum observed for III (IIIb, ν(CO) 1955(s), 1891(s) and 1759(m,br) cm^{-1}) is consistent with the formulation of these derivatives as $(\mu\text{-}C_7H_7)(\mu\text{-}CO)\text{-}\overline{Fe}(CO)_2\overline{Rh}(PR_3)_2$. Since the parent molecule, I, did not contain a bridging carbonyl group and since the above formulation requires a reversal of the bonding mode of the $\mu\text{-}C_7H_7$ moiety on the Rh—Fe framework upon PR_3 substitution, a single crystal X-ray structural study*** on III was deemed necessary (Fig. 1).

(I)   2 PR$_3$ →   (3)

(OC)$_2$Rh——Fe(CO)$_3$ (OC)$_2$Fe——Rh(PR$_3$)$_2$

(III)

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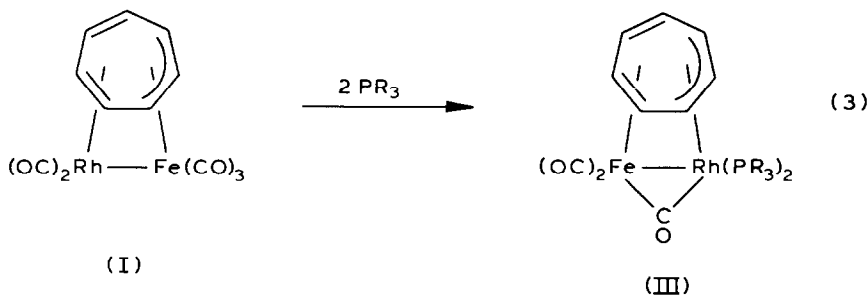
*We have recently observed that in solution IIIc isomerizes to the dppm bridged compound.

**All new compounds gave satisfactory elemental analysis. Selected spectroscopic data: IR, ν(CO) (cm^{-1}) (CH$_2$Cl$_2$): IIa 2000(s), 1967(s), 1912(s), 1790(m); IIb 2000(s), 1971(s), 1930(s), 1802(m); IIIa 1948(s), 1879(s), 1742(m); IIIb 1955(s), 1891(s), 1759(m); IIIc 1956(s), 1891(s), 1758(m); ^{1}H NMR, δ (ppm) (CD$_2$Cl$_2$): IIb 7.53—7.40 (m, C$_6$H$_5$), 3.84 (s, C$_7$H$_7$); IIIb 7.71—7.24 (m, C$_6$H$_5$), 3.80 (s, C$_7$H$_7$), 2.75 (br, CH$_2$), 2.15 (br, CH$_2$); IIIc 7.36 (br, C$_6$H$_5$), 4.30 (t, CH$_2$), 4.04 (s, C$_7$H$_7$); ^{13}C NMR, δ(CO) (ppm) (CD$_2$Cl$_2$): IIb (−30°C) 227.44 (d, Fe—CO, J(P—C) 7.1 Hz), 201.58 (dd, Rh—CO, J(Rh—C) 84.5, J(P—C) 18.5 Hz); IIIb (−80°C) 261.38 (d, μ-CO, J(Rh—C) 26.7 Hz), 227.07 (s, Fe—CO); IIIc (−80°C) 258.82 (s, br, μ-CO), 228.19 (s, Fe—CO); ^{31}P NMR, δ (ppm) (CD$_2$Cl$_2$): IIb 43.9 (d, J(Rh—P) 179.3 Hz); IIIb 67.43 (d, J(Rh—P) 178.2 Hz); IIIc −14.34 (d, J(Rh—P) 152.3 Hz).

***Crystal data: RhFeP$_2$O$_3$C$_{36}$H$_{31}$; space group $I2/a$, a 22.496(4), b 10.695(3), c 27.362(3) Å, β 111.17(1)°; $Z = 16$, ρ_c 1.582 g/cm^3. The structure was solved and refined using 2206 observed reflections ($I > 3\sigma(I)$) measured on an Enraf—Nonius CAD4 automated diffractometer using Mo-K_α radiation. With anisotropic parameters for all non-hydrogen and phenyl carbon atoms the R and R_w values were 0.057 and 0.066, respectively.
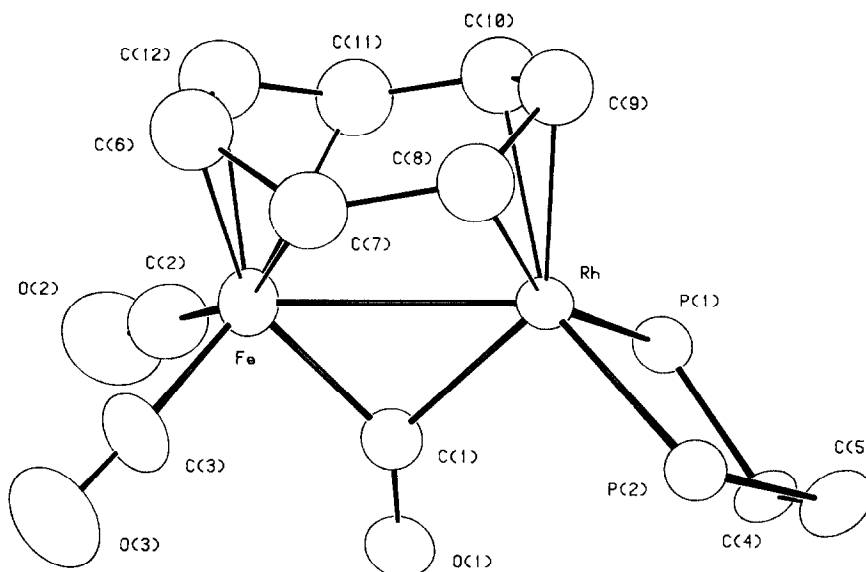
Fig. 1. A perspective of the molecular structure of (μ-C$_7$H$_7$)(μ-CO)Fe(CO)$_2$Rh(dppe), phenyl groups omitted for clarity. Relevant distances (Å): Rh—Fe 2.762(2), Fe—C(7) 2.23(1), Fe—C(11) 2.30(1), Fe—C(6) 2.07(1), Fe—C(12) 2.09(1), Rh—C(8) 2.25(1), Rh—C(10) 2.24(1), Rh—C(9) 2.20, Fe—C(1) 1.93, Rh—C(1) 2.05.

It is evident that the solid state structure corroborates the above prediction. The distances in III closely resemble those found in I [5] and in particular the Fe—Rh bond length remains virtually identical (I, Fe—Rh 2.764(1) Å). The observation of two structural types, I and III, clearly establishes the ability of the C$_7$H$_7$ moiety to accommodate, under certain conditions, different bonding requirements of metal carbonyl fragments*. This and its ability of providing momentary unsaturation at metal centers may have important bearing on the reactivity of I and related C$_7$H$_7$ derivatives.

References

1 J.K. Kochi. Organometallic Mechanisms and Catalysis, Academic Press, New York, 1978.
2 M. Tsutsui and A. Courtney, Adv. Organometal. Chem., 16 (1977) 241.
3 C.P. Casey, J.M. O'Connor, W.D. Jones and K.J. Haller, Organometallics, 2 (1983) 535 and references therein.
4 H.G. Shuster-Woldan and F. Basolo, J. Am. Chem. Soc., 88 (1966) 1657.
5 M.J. Bennett, J.L. Pratt, K.A. Simpson, L.K.K. LiShingMan and J. Takats, J. Am. Chem. Soc., 98 (1976) 4810.

*Variable bonding of C$_7$H$_7$ in mononuclear metal carbonyls is known also: (a) J.G.A. Reuvers and J. Takats, submitted for publication, (b) G.-Y. Lin, unpublished observations.