Synthesis and Chemistry of Cycloheptatrienyltricarbonylruthenate(1−), $[(\eta^3\text{-}C_7H_7)Ru(CO)_3]^-$

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Controlled deprotonation of (cycloheptatriene)tricarbonylruthenium (**1**) yields the anionic complex $[(\eta^3\text{-}C_7H_7)Ru(CO)_3]^-$ (**2**) which reacts with Ph_3SnCl to give fluxional $(\eta^3\text{-}C_7H_7)Ru(CO)_3SnPh_3$ and $(\eta^5\text{-}C_7H_7)Ru(CO)_2SnPh_3$, and which can be converted into the cycloheptatrienyl bridged heterobimetallic complexes $(\mu\text{-}C_7H_7)Ru(CO)_3RhL_2$ (L_2 = cyclo-octadiene, 2CO).

The reaction of metal carbonyl anions with electrophiles is one of the fundamental strategies for the preparation of new organometallic complexes.[1] We[2] and others[3,4] have shown that the ambident organometallic nucleophile, $[(\eta^3\text{-}C_7H_7)Fe(CO)_3]^-$, is particularly interesting in this regard since, depending on the electrophile used, ring substituted compounds, $(\eta^4\text{-}C_7H_7R)Fe(CO)_3$ (R = $SiMe_3$, $GeMe_3$, $GePh_3$),[2a] or metal bonded species, $(\eta^y\text{-}C_7H_7)Fe(CO)_xSnPh_3$ ($x = 3, y = 3; x = 2, y = 5$)[2c] and $(\mu\text{-}C_7H_7)Fe(CO)_3ML_2$ [M = Rh, Ir; L_2 = 2CO, cyclo-octadiene (cod)],[2b] can be obtained. The latter class of compounds represents interesting examples of cycloheptatrienyl bridged heterobimetallic complexes which exhibit facile CO substitution processes.[5] With a view to probe the metal dependence of the fluxional behaviour and reactivity characteristics of cycloheptatrienyl based compounds, the synthesis and derivatization of the analogous $(\eta^3\text{-}C_7H_7)Ru(CO)_3^-$ has been explored.

Contrary to the deprotonation of (cycloheptatriene)tricarbonyliron, $(\eta^4\text{-}C_7H_8)Fe(CO)_3$, which can be achieved with a variety of strong bases,[2—4] the reaction of the analogous ruthenium compound† requires considerably more care. Although deprotonation of (**1**) with $KOBu^t$ proceeds rapidly and gives exclusively the desired anion (**2**), Scheme 1, the reaction with KH or $NaN(SiMe_3)_2$ results in a mixture of mono- and di-nuclear anionic species as shown by subsequent

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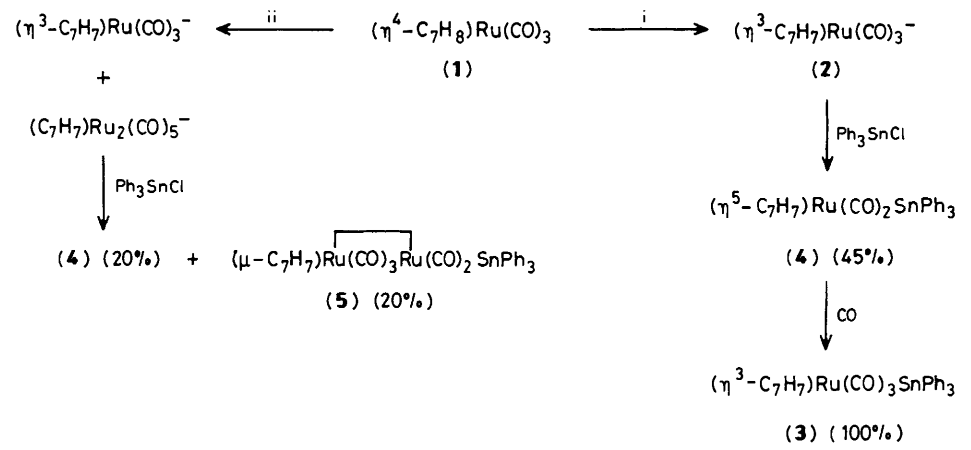
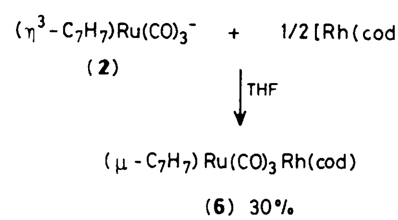
† $(\eta^4\text{-}C_7H_8)Ru(CO)_3$ (**1**) was obtained by modification of the published procedure.[6] Photolysis (450 W, high pressure Hanovia mercury lamp) of $Ru_3(CO)_{12}$ and excess of cycloheptatriene in benzene at 70 °C gave an 80—85% isolated yield of (**1**).



Scheme 1. i, $KOBu^t$/tetrahydrofuran(THF); ii, KH/THF or $NaN(SiMe_3)_2$/toluene.

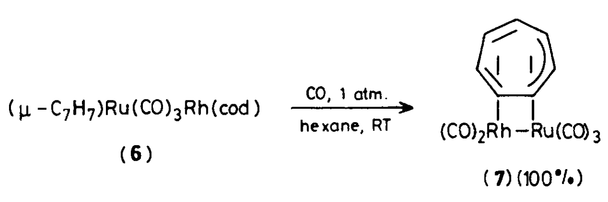


(1)

reaction with Ph_3SnCl.‡ Unexpectedly, the primary product of the reaction between (**2**) and Ph_3SnCl is the η^5-bonded cycloheptatrienyl complex, $(\eta^5\text{-}C_7H_7)Ru(CO)_2SnPh_3$ (**4**) resulting from ready CO loss from either (**2**) and/or (**3**) during the course of the reaction. The η^3-bonded complex, $(\eta^3\text{-}C_7H_7)Ru(CO)_3SnPh_3$ (**3**), is readily obtained from (**4**) by atmospheric pressure carbonylation at room temperature. This step is reversible thereby establishing the facility of the CO addition and elimination reactions in compounds (**4**) and (**3**). Not surprisingly, both compounds are fluxional in solution; the nature and energetics of the rearrangements will be the subject of a full report.

Anion (**2**) also reacts with $[Rh(cod)Cl]_2$ to give, in a straightforward fashion, the heterobimetallic complex (**6**), equation (1).

Although the yield of (**6**) is lower than in the analogous iron reaction, the compound, as before,[5] is readily and quantitatively carbonylated to the corresponding pentacarbonyl (**7**), equation (2).



(2)

The latter compound reacts smoothly with one equivalent of PPh_3 to give $(\mu\text{-}C_7H_7)Ru(CO)_3Rh(CO)(PPh_3)$ (**8**), the CO substitution occurring preferentially at the rhodium centre. We have attributed the facility of the CO substitution reactions to the incipient co-ordinative unsaturation provided by the flexible bonding capability of the $\mu\text{-}C_7H_7$ moiety.[5]

In conclusion, we have shown that $[(\eta^3\text{-}C_7H_7)Ru(CO)_3]^-$ provides a convenient entry into a variety of reactive cycloheptratrienyl–ruthenium derivatives. Further reactions of these compounds and detailed comparison to the related iron complexes will form the basis of future reports.

We thank N.S.E.R.C. (Canada) and the University of Alberta for financial support of this work. F. E. acknowledges a Feodor Lynen research fellowship from the Alexander von Humboldt Foundation, Bonn, West Germany.

Received, 22nd October 1987; Com. 1538

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‡ *Selected data* for new complexes: satisfactory elemental analyses have been obtained for all isolated compounds. Characteristic CO stretching frequencies (ν_{CO}, cm^{-1}) are: (**2**) in THF: 1959s, br, 1886s, br, 1864sh; (**3**): 2065s, 2013s, 1989s; (**4**): 2023s, 1976s; (**5**): 2065s, 2012s, 2004s, 1986m, 1959m, all in hexane. (**6**), bright red, crystalline solid: i.r. (ν_{CO}, cm^{-1}, hexane) 2029s, 1965s; ^{13}C n.m.r. (δ, CD_2Cl_2) 63.1 (s, C_7H_7), 80.9 (d, CH, J_{Rh-C} 9.2 Hz), 32.4 (s, CH_2), 201.6 (s, CO). (**7**), bright red solid: i.r. (ν_{CO}, cm^{-1}, hexane) 2064s, 2023s, 2004s, 1979s; ^{13}C n.m.r. (δ, p.p.m., $C_6D_5CD_3$) 61.3 (s, C_7H_7), 194.9 (d, CO_{Rh}, J_{Rh-C} 72 Hz), 200.6 (s, CO_{Ru}). (**8**), red solid: i.r. (ν_{CO}, cm^{-1}, CD_2Cl_2) 2009s, 1982s, 1941s, 1809m; ^{13}C n.m.r. (δ, CD_2Cl_2, −30 °C) 65.1 (s, C_7H_7), 137—135 (C_6H_5), 202.5 (dd, CO_{Rh}, J_{Rh-C} 87.8, J_{P-C} 15.8 Hz), 217.0 (s, CO_{Ru}); ^{31}P n.m.r. (δ, CD_2Cl_2) 40.88 (d, J_{Rh-P} 183.3 Hz).

References

1 R. B. King, *Acc. Chem. Res.*, 1970, **3**, 417; J. E. Ellis, *J. Organomet. Chem.*, 1975, **86**, 1.

2 (a) L. K. K. LiShingMan, J. G. A. Reuvers, J. Takats, and G. Deganello, *Organometallics*, 1983, **2**, 28; (b) M. J. Bennett, J. L. Pratt, K. A. Simpson, L. K. K. LiShingMan, and J. Takats, *J. Am. Chem. Soc.*, 1976, **98**, 4810; F. Edelmann and J. Takats, *J. Organomet. Chem.*, in the press; (c) J. G. A. Reuvers and J. Takats, manuscript in preparation.

3 M. Moll, H. Behrens, R. Kellner, H. Knöchel, and P. Würstl, *Z. Naturforsch., Teil B*, 1976, **31**, 1019; H. Behrens, K. Geibel, R. Kellner, H. Knöchel, and E. Sepp, *ibid.*, 1976, **31**, 1021.

4 G. Deganello, T. Boschi, and L. Toniolo, *J. Organomet. Chem.*, 1975, **97**, C46; M. Airoldi, G. Deganello, G. Dia, P. Saccone, and J. Takats, *Inorg. Chim. Acta*, 1980, **41**, 171.

5 R. G. Ball, F. Edelmann, G.-Y. Kiel, J. Takats, and R. Drews, *Organometallics*, 1986, **5**, 829.

6 J. C. Burt, S. A. R. Knox, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1975, 731.