Synthesis of Mono-η-benzenebis(trimethylphosphine)-manganese and -rhenium Compounds Using the Metal Atoms

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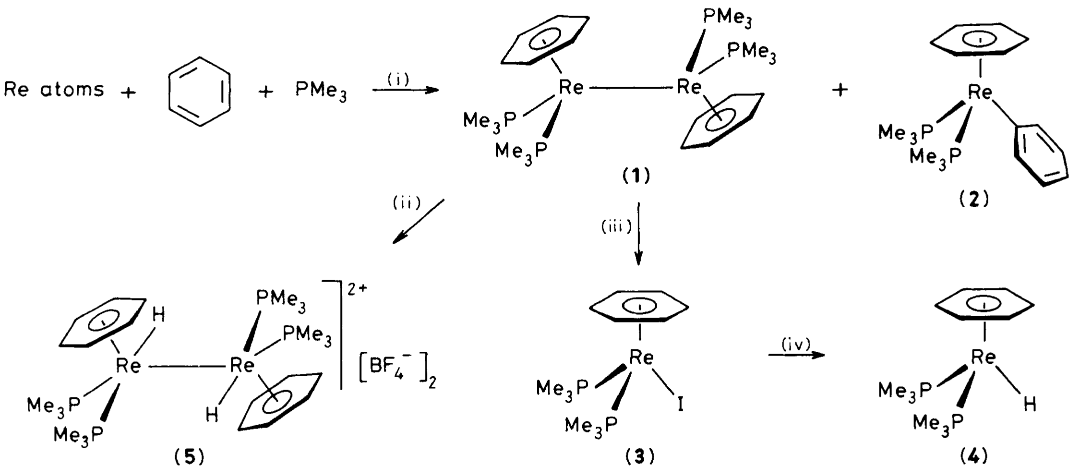
Co-condensation of manganese or rhenium atoms with a mixture of benzene and trimethylphosphine forms the compounds $Mn(\eta\text{-}C_6H_6)(PMe_3)_2H$ and $[Re(\eta\text{-}C_6H_6)(PMe_3)_2]_2$ respectively; the latter gives rise to the derivatives $Re(\eta\text{-}C_6H_6)(PMe_3)_2R$ (R = I or H).

We have previously shown that co-condensation of atoms of zirconium or hafnium with a benzene–trimethylphosphine mixture forms the mixed ligand compounds $M(\eta\text{-}C_6H_6)_2(PMe_3)$ (M = Zr of Hf) in moderate yields.[1] Tolman and Ittel have recently described thermally sensitive mono-arene-iron derivatives including the compound $Fe(\eta\text{-}C_6H_5Me)(PMe_3)_2$. The latter was made by addition of trimethylphosphine to the product formed by co-condensation of iron with toluene.[2] Here we describe the synthesis and properties of new mono-arene derivatives of rhenium and manganese using the mixed ligand co-condensation approach.

In a typical experiment, rhenium atoms (4.1 g), vapourised from a positive hearth electron gun furnace[3,4] were co-condensed with benzene and trimethylphosphine (120 cm^3 of a 5:1 mixture) over a period of 4 h. Removal of the excess of benzene and trimethylphosphine under reduced pressure followed by chromatography and crystallisation gave as the main product orange crystals of the compound $[Re(\eta\text{-}C_6H_6)(PMe_3)_2]_2$ (**1**) in 30% yield (based on rhenium evaporated from the furnace). Chromatography separated as a minor product (*ca.* 2%) the yellow crystalline compound $Re(\eta\text{-}C_6H_6)(PMe_3)_2Ph$ (**2**).

The photoelectron spectrum of (**1**) has a lowest ionisation band at 6.06 eV showing it to be a high-energy compound.[5,6] The Re–Re bond of (**1**) may not be cleaved by sodium amalgam in tetrahydrofuran (THF). However, treatment of (**1**) in THF with a potassium film leads to the formation of a deep red solution which with methyl iodide forms the orange iodo derivative $Re(\eta\text{-}C_6H_6)(PMe_3)_2I$ (**3**). The red solution presumably contains the anion $[Re(\eta\text{-}C_6H_6)(PMe_3)_2]^-$. Treatment of (**3**) with lithium tetrahydridoaluminate gives the yellow hydrido derivative $Re(\eta\text{-}C_6H_6)(PMe_3)_2H$ (**4**). The basic character of (**1**) is demonstrated by its reaction with proton acids forming the di-hydrido cation $[Re(\eta\text{-}C_6H_6)(PMe_3)_2H]_2[BF_4]_2$ (**5**).

Co-condensation of manganese with a benzene–trimethylphosphine mixture, as described above for rhenium, gives as dark red crystals from light petroleum (b.p.



Scheme 1. *Reagents and conditions:* (i) Co-condensation at −195 °C, 40% (**1**), 2% (**2**); (ii) aq. HBF_4, >90%; (iii) K mirror, naphthalene (trace) in tetrahydrofuran, >90%, then methyl iodide in tetrahydrofuran, >90%; (iv) $LiAlH_4$ in tetrahydrofuran, *ca.* 70%.

30—40 °C) the hydrido compound $Mn(\eta\text{-}C_6H_6)(PMe_3)_2H$ (**6**); typically 8.0 g of condensed manganese metal atoms gave 0.75 g of (**6**).

The new compounds (**1**)—(**6**) have been fully characterised by microanalysis, mass spectroscopy where appropriate, and especially by their n.m.r. spectra.†

It is clear that the mono-arene-manganese and -rhenium compounds are thermally stable and reactive and that they will have an extensive chemistry. Manganese is easy to volatilise (950 °C) and, despite the relatively low yields of reactions involving manganese atoms,[7] it seems that they can act as a useful synthetic intermediate with suitable ligands.

We thank the S.E.R.C. for support (J.M.W.), the Northern Ireland Department of Education and B.P., p.l.c., for support (D.O'H) and the Donors of the Petroleum Research Fund administered by the American Chemical Society for partial support.

Received, 18th November 1983; Com. 1556

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† N.m.r. data, J in Hz, in C_6H_6 unless otherwise stated: for (**1**), ^1H δ 4.26 (s, 12H, $2\eta\text{-}C_6H_6$) and 1.23 (filled-in doublet, 36H, $4PMe_3$); $^{31}P\{^1H\}$, −45.8 p.p.m. (s, $4PMe_3$); for (**2**), ^1H, δ 7.74 (complex, 2H, *o*-H), 7.08 (complex, 3H, *m*- and *p*-H), 4.02 (t, 6H, $^3J_{P\text{-}H}$ 1.5, $\eta\text{-}C_6H_6$), and 1.16 (filled-in doublet, 18H, $2PMe_3$); $^{31}P\{^1H\}$, −46.7 p.p.m. (s, $2PMe_3$); $^{13}C\{^1H\}$, δ 23.5 (t, 6C, $^1J_{P\text{-}C}$ 15.1, $2PMe_3$), 72.9 (t, 6C, $^2J_{P\text{-}C}$ 2.08, $\eta\text{-}C_6H_6$), 120.0 (s, 1C *p*-C), 126.1 (s, 2C, *m*-C), and 144.2 p.p.m. (t, 2C, $^3J_{P\text{-}C}$ 6.8, *o*-C); for (**3**), ^1H, δ 4.23 (t, 6H, $^3J_{P\text{-}H}$ 1.7, $\eta\text{-}C_6H_6$) and 1.33 (filled-in doublet, 18H, $2PMe_3$); $^{31}P\{^1H\}$, δ −61.7 p.p.m. (s, $2PMe_3$); for (**4**), ^1H, 4.28 (s, 6H, $\eta\text{-}C_6H_6$), 1.39 (filled-in doublet, 18H, $2PMe_3$) and −8.70 (t, 1H, $^2J_{P\text{-}H}$ 36.8, ReH); $^{31}P\{^1H\}$, δ −45.5 p.p.m. (s, $2PMe_3$); for (**5**) in $(CD_3)_2CO$ ^1H, δ 6.06 (s, 12H, $2\eta\text{-}C_6H_6$), 1.87 (filled-in doublet, 36H, $4PMe_3$) and −8.74 (t, 2H, $^2J_{P\text{-}H}$ 48.1, 2ReH); $^{31}P\{^1H\}$, δ −36.6 p.p.m. (s, $4PMe_3$); for (**6**) ^1H, δ 4.36 (s, 6H, $\eta\text{-}C_6H_6$), 1.04 (filled-in doublet, 18H, $2PMe_3$) and −10.39 (t, 1H, $^2J_{P\text{-}H}$ 82.8, MnH); $^{31}P\{^1H\}$ 24.3 p.p.m. (s, $2PMe_3$).

References

1 F. G. N. Cloke and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1981, 1938.
2 S. D. Ittel and C. A. Tolman, *Organometallics*, 1982, **1**, 1432.
3 M. L. H. Green, 'Frontiers of Chemistry,' IUPAC, ed. K. J. Laidler, Pergamon, Oxford, 1982, p. 229.
4 M. L. H. Green, *J. Organomet. Chem.*, 1980, **200**, 119.
5 J. C. Green, *Struct. Bonding (Berlin)*, 1981, **43**, 37.
6 J. C. Green and R. R. Watson, personal communication.
7 E. P. Kundig, P. L. Timms, B. A. Kelly, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 901 and references therein.