

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 $\text{Mn}(\eta\text{-C}_6\text{H}_6)(\text{PMe}_3)_2\text{H}$ and $[\text{Re}(\eta\text{-C}_6\text{H}_6)(\text{PMe}_3)_2]_2$ respectively; the latter gives rise to the derivatives $\text{Re}(\eta\text{-C}_6\text{H}_6)(\text{PMe}_3)_2\text{R}$ (R = I or H).

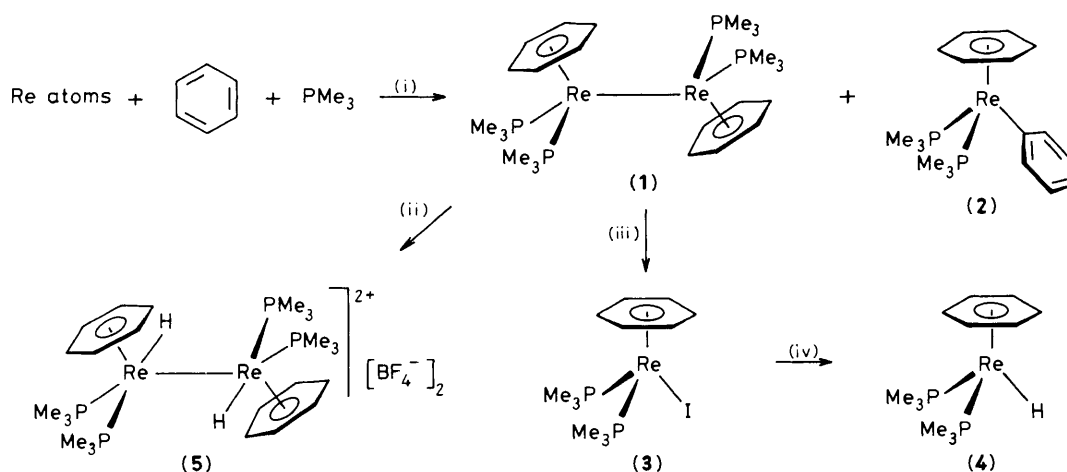
We have previously shown that co-condensation of atoms of zirconium or hafnium with a benzene-trimethylphosphine mixture forms the mixed ligand compounds $\text{M}(\eta\text{-C}_6\text{H}_6)_2(\text{PMe}_3)$ (M = Zr or Hf) in moderate yields.¹ Tolman and Ittel have recently described thermally sensitive mono-arene-iron derivatives including the compound $\text{Fe}(\eta\text{-C}_6\text{H}_5\text{Me})(\text{PMe}_3)_2$. 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 cm³ 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 $[\text{Re}(\eta\text{-C}_6\text{H}_6)(\text{PMe}_3)_2]_2$ (**1**) in 30% yield (based on rhenium evapor-

ated from the furnace). Chromatography separated as a minor product (*ca.* 2%) the yellow crystalline compound $\text{Re}(\eta\text{-C}_6\text{H}_6)(\text{PMe}_3)_2\text{Ph}$ (**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 $\text{Re}(\eta\text{-C}_6\text{H}_6)(\text{PMe}_3)_2\text{I}$ (**3**). The red solution presumably contains the anion $[\text{Re}(\eta\text{-C}_6\text{H}_6)(\text{PMe}_3)_2]^-$. Treatment of (**3**) with lithium tetrahydridoaluminate gives the yellow hydrido derivative $\text{Re}(\eta\text{-C}_6\text{H}_6)(\text{PMe}_3)_2\text{H}$ (**4**). The basic character of (**1**) is demonstrated by its reaction with proton acids forming the di-hydrido cation $[\text{Re}(\eta\text{-C}_6\text{H}_6)(\text{PMe}_3)_2\text{H}]_2[\text{BF}_4]_2$ (**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%.

$30\text{--}40^\circ\text{C}$) the hydrido compound $\text{Mn}(\eta\text{-C}_6\text{H}_6)(\text{PMe}_3)_2\text{H}$ (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.

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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.

[†] N.m.r. data, J in Hz, in C_6H_6 unless otherwise stated: for (1), ^1H δ 4.26 (s, 12H, $2\eta\text{-C}_6\text{H}_6$) and 1.23 (filled-in doublet, 36H, 4PMe_3); $^{31}\text{P}\{^1\text{H}\}$, δ -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, $^3J_{\text{P-H}}$ 1.5, $\eta\text{-C}_6\text{H}_6$), and 1.16 (filled-in doublet, 18H, 2PMe_3); $^{31}\text{P}\{^1\text{H}\}$, δ -46.7 p.p.m. (s, 2PMe_3); $^{13}\text{C}\{^1\text{H}\}$, δ 23.5 (t, 6C, $^1J_{\text{P-C}}$ 15.1, 2PMe_3), 72.9 (t, 6C, $^2J_{\text{P-C}}$ 2.08, $\eta\text{-C}_6\text{H}_6$), 120.0 (s, 1C *p*-C), 126.1 (s, 2C, *m*-C), and 144.2 p.p.m. (t, 2C, $^3J_{\text{P-C}}$ 6.8, *o*-C); for (3), ^1H , δ 4.23 (t, 6H, $^3J_{\text{P-H}}$ 1.7, $\eta\text{-C}_6\text{H}_6$) and 1.33 (filled-in doublet, 18H, 2PMe_3); $^{31}\text{P}\{^1\text{H}\}$, δ -61.7 p.p.m. (s, 2PMe_3); for (4), ^1H , 4.28 (s, 6H, $\eta\text{-C}_6\text{H}_6$), 1.39 (filled-in doublet, 18H, 2PMe_3) and -8.70 (t, 1H, $^2J_{\text{P-H}}$ 36.8, ReH); $^{31}\text{P}\{^1\text{H}\}$, δ -45.5 p.p.m. (s, 2PMe_3); for (5) in $(\text{CD}_3)_2\text{CO}$ ^1H , δ 6.06 (s, 12H, $2\eta\text{-C}_6\text{H}_6$), 1.87 (filled-in doublet, 36H, 4PMe_3) and -8.74 (t, 2H, $^2J_{\text{P-H}}$ 48.1, 2ReH); $^{31}\text{P}\{^1\text{H}\}$, δ -36.6 p.p.m. (s, 4PMe_3); for (6) ^1H , δ 4.36 (s, 6H, $\eta\text{-C}_6\text{H}_6$), 1.04 (filled-in doublet, 18H, 2PMe_3) and -10.39 (t, 1H, $^2J_{\text{P-H}}$ 82.8, MnH); $^{31}\text{P}\{^1\text{H}\}$ 24.3 p.p.m. (s, 2PMe_3).