Formation of a Rhenium Benzyne Derivative by Facile Ligand-induced *ortho*-Hydrogen Abstraction in a Homoleptic Rhenium Aryl; *X*-Ray Crystal Structure of $Re(\eta^2\text{-}2\text{-}MeC_6H_3)(2\text{-}MeC_6H_4)_2(PMe_2Ph)_2$

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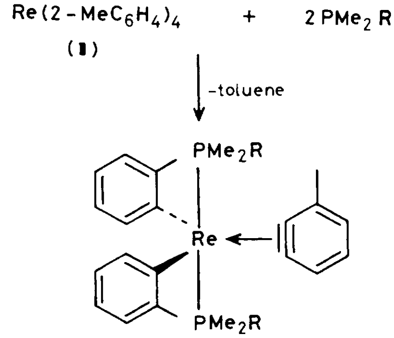
The rhenium benzyne complexes $Re(\eta^2\text{-}2\text{-}MeC_6H_3)(2\text{-}MeC_6H_4)_2(PMe_2R)_2$(R = Me or Ph) are formed at low temperature by reaction of $Re(2\text{-}MeC_6H_4)_4$ with PMe_2R; the PMe_2Ph derivative has been characterized by *X*-ray crystallography.

An important aspect of organometallic chemistry is the stabilization on a transition metal centre of organic fragments that are normally highly reactive in the free, uncomplexed state.[1] To date, however, there are few reported examples of structurally characterized mononuclear transition metal complexes containing the benzyne moiety.[2] The decomposition of many transition metal aryl complexes is thought to proceed *via* benzyne intermediates generated by *ortho*-hydrogen abstraction from the aryl ligand.[2a—c,3] In a few instances stable metal η^2-benzyne derivatives are formed, although this often requires prolonged thermolysis of the metal aryl starting material at elevated temperatures.[2a—c] The benzyne moiety in these compounds has been found to be quite reactive;[2] metal–benzyne derivatives may be useful reagents in organic synthesis.[4]

The first studies on stable homoleptic aryls have led to a remarkably facile synthesis of the only example of a rhenium–benzyne complex. Treatment of the *o*-tolyl derivative $Re(2\text{-}MeC_6H_4)_4$ (**1**)[5] with 2 equiv. of PMe_3 or PMe_2Ph in cold (−40 °C) toluene results in a rapid colour change from black to maroon (Scheme 1). The complexes (**2**) were isolated in almost quantitative yield as dark maroon air-stable crystals from cold hexane;† the formulation as monomeric benzyne derivatives has been confirmed unequivocally by single-crystal *X*-ray diffraction studies.‡



(**2**)**a**; R = Me **b**; R = Ph

Scheme 1

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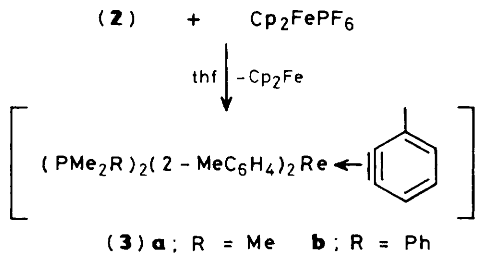
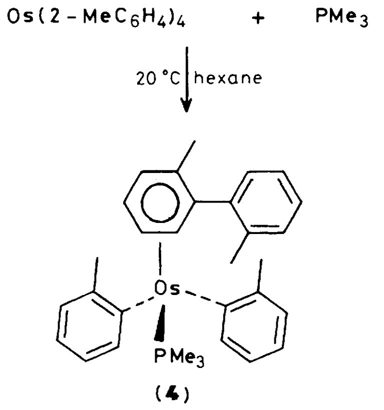
† Satisfactory elemental analyses have been obtained for all compounds. For (**2a**): 91% yield; m.p. 165—166 °C; *m/z* 611(M^+); magnetic moment 1.60(5) B.M. (Evans' method in benzene; 25 °C). For (**3a**): 93% yield; m.p. 218—219 °C. Selected n.m.r. data: $^{13}C\{^1H\}$ [62.9 MHz; $(CD_3)_2CO$; 20 °C] δ 165.9 (d, J_{PC} 25 Hz) and 169.0 (d, J_{PC} 30 Hz) (benzyne C-5, C-6); $^{31}P\{^1H\}$ (36.3 MHz; $CDCl_3$; 20 °C; ref. H_3PO_4) δ 22.9 and 30.3 (ABq, $|J|$ 128 Hz).

‡ *Crystal data* for (**2b**): $C_{37}H_{24}P_2Re$, triclinic, $P\bar{1}$, $a = 9.987(3)$, $b = 17.160(3)$, $c = 10.761(3)$ Å, $\alpha = 105.87(2)°$, $\beta = 111.15(3)°$, $\gamma = 90.91(2)°$, $V = 1640.09$ Å^3, $Z = 2$, $D_c = 1.487$ g cm^{-3}, $\mu = 38.4$ cm^{-1}, $F(000) = 738$. Data recorded with a CAD-4 diffractometer in $\omega/2\theta$ scan mode with monochromated Mo-K_α radiation and corrected for absorption; 6139 data measured ($1.5° < \theta < 25°$), 5753 unique, 4655 used [$I > 1.5\sigma I$]. The structure was solved *via* heavy atom procedures refined by least-squares with hydrogens isotropic, non-hydrogens anisotropic, to $R = 0.030$, $R_w = 0.028$ for 198 parameters. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 2



Scheme 3

Assuming that the benzyne ligand occupies a single co-ordination site, the structure of (**2b**) is best described as a distorted trigonal bypyramid with axial phosphines (Figure 1). The C(51)–C(52) benzyne bond length [1.342(10) Å] is close to that in the related complex $Ni(\eta^2-C_6H_4)(Cy_2PCH_2CH_2PCy_2)$[1.332(6) Å].[2d] Compared with the two *o*-tolyl ligands, however, the remaining parameters in the η^2-benzyne moiety are almost identical. Of the Re–C distances, the two to the benzyne ligand [av. 2.035(6) Å] are somewhat shorter than those to the σ-bonded $2-MeC_6H_4$ groups [av. 2.117(7) Å]. These values are to be compared with Re–C distances in $Re(2-MeC_6H_4)_4$ (**1**) [2.030(9) Å][5] and the acetylene complex $Re(O)I(MeCCMe)_2$ [from 2.038(5) to 2.066(5) Å].[6] Our data, therefore, appear consistent with a rhenacyclopropene-type structure and delocalized, aromatic benzyne ligand.

These neutral paramagnetic compounds are readily oxidized to the dark red diamagnetic cations (**3**) (Scheme 2). Following re-crystallization from dichloromethane–diethyl ether, the salts (**3**) were obtained as air- and moisture-stable crystals in >90% yield. Preliminary *X*-ray data indicate that the gross structural features of the cation in (**3a**) (as the BPh_4^- salt) are analogous to those in the neutral precursor. N.m.r. data similarly support the proposed structure; in addition the observation of inequivalent phosphines but identical *o*-tolyl ligands suggests that rotation about the Re–benzyne bond is slow on the n.m.r. time scale at 25 °C.

Present results suggest that these benzyne complexes are remarkably thermally stable and rather inert. For example, (**3a**) is unreactive towards CO, H_2, C_2H_4, C_2H_2, $Me_3SiCCSiMe_3$, and MeI (all >3 equiv.; 60 °C, 24 h, in $CDCl_3$ solution) and neat acetonitrile or acetone (up to 70 °C; 2 days).

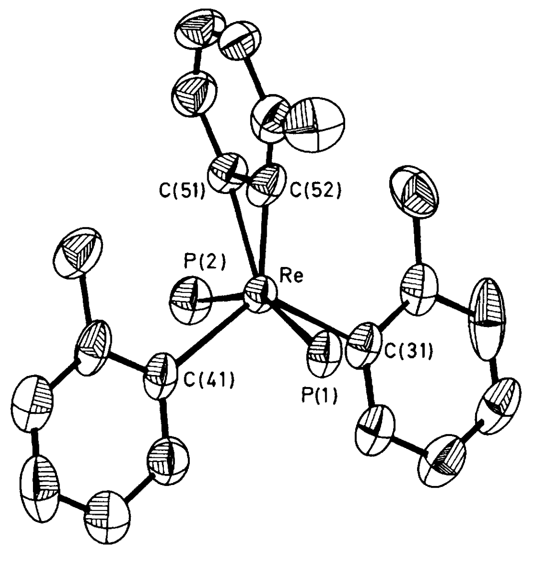


Figure 1. Molecular structure of $Re(\eta^2-2-MeC_6H_3)(2-MeC_6H_4)_2(PMe_2Ph)_2$ (**2b**), showing atom-labelling scheme; methyl and phenyl groups on phosphorus have been omitted for clarity; selected bond lengths (Å) and angles(°): C(51)–C(52) 1.342(10), Re–C(51) 2.026(7), Re–C(52) 2.046(6), Re–C(31) 2.120(7), Re–C(41) 2.115(7), Re–P(1) 2.431(4), Re–P(2) 2.407(4), P(1)–Re–P(2) 153.5(3), C(31)–Re–C(41) 118.7(3), C(41)–Re–C(51) 114.2(3), C(41)–Re–C(52) 114.8(3), C(51)–Re–C(52) 38.5(2).

We are now studying similar chemistry of other homoleptic aryls of transition metals. For the analogous $Os(2-MeC_6H_4)_4$,[7] however, reductive coupling of aryl groups on the transition metal is the preferred reaction pathway (Scheme 3). The π-arene structure of (**4**), obtained as yellow crystals in 94% yield, has been confirmed by *X*-ray crystallography. Detailed mechanistic and reactivity studies are in progress.

Note added in proof: The crystal structures of two niobium and tantalum bis-benzyne complexes are now available: R. A. Bartlett, P. P. Power, and S. C. Schoner, *J. Am. Chem. Soc.*, 1988, **110**, 1966.

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