# An Orthometallated Cyclopentadienyl Phosphine Bridge in a New Type of Heterobimetallic Complex: $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4)Mo\{o\text{-}C_6H_4P(Ph)Cr(CO)_5\}]X$ (X = Cl, I)

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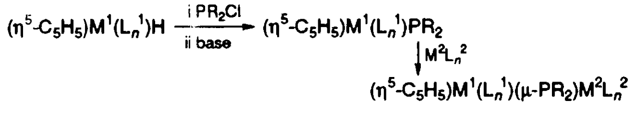
An unexpected product is obtained during the reaction between $(\eta^5\text{-}C_5H_5)_2MoCl_2$ and $Li[Cr(CO)_5(PPh_2)]$ resulting in the formation of a dinuclear complex with the novel $[(\eta^5\text{-}C_5H_4)PPh\{Cr(CO)_5\}C_6H_4]$ ligand; the crystal structure of one derivative is reported.

Linking divergent transition metal centres with bridging ligands allows interaction between them, leading to potentially novel properties.[1] We have recently investigated a class of μ-phosphido-heterobimetallic complexes incorporating a Group 5 or 6 metallocene derivative and a Group 6–8 transition metal carbonyl moiety.[2] A traditional method for preparing such bimetallic compounds involves formation of a donor–acceptor phosphorus–metal bond from a metallophosphane complex to a metal atom of an electron-unsaturated species as outlined in Scheme 1. Metallophosphanes can be obtained from the corresponding metallocene hydride complexes.

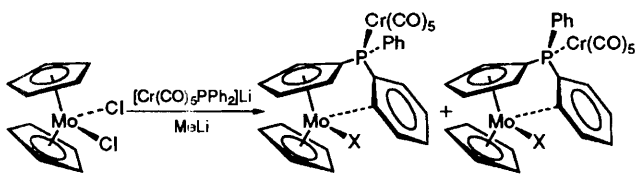
This versatility is especially valuable in the construction of extended molecular systems. In order to prepare the bisphosphido trimetallic complex $[(\eta^5\text{-}C_5H_5)Mo\{PPh_2Cr(CO)_5\}_2]$, two approaches have been studied. The first route consists in appending $LiPPh_2$ to $[(\eta^5\text{-}C_5H_5)_2MoCl_2]$ prior to metal complexation; but the complexity of the reaction mixture does not permit isolation of the desired product. The second utilizes the metallated phosphide $Li[Cr(CO)_5(PPh_2)]$. This communication reports on synthesis, characterisation and X-ray structure analysis of an unexpected cyclopentadienyl-substituted and *ortho*-metallated bimetallic complex formed by the latter method.

Complex **1** (Scheme 2) was prepared in a single step by rapid addition of $Li[Cr(CO)_5(PPh_2)]$[3] [prepared *in situ* from $HPPh_2\text{–}Cr(CO)_5$ and MeLi] to $[(\eta^5\text{-}C_5H_5)_2MoCl_2]$ suspended in THF, followed by chromatographic work-up. The composition was determined by elemental analysis and FD MS and **1** was characterized spectroscopically.†

The cyclopentadienyl ring substitution and the *ortho*-metallation were confirmed by a combination of $^1H$, $^{13}C$ and $^{31}P$ NMR and IR spectroscopy. The major feature of the $^1H$ NMR spectrum for complex **1** is the non-equivalence of the cyclopentadienyl protons that are adjacent to the newly generated chiral phosphorus centre. The $^{13}C$ NMR data are also consistent with the designated structure: the aryl-carbon region of the spectrum shows the presence of three quaternary carbon atoms (δ 136, 157.4 and 170.7).



Scheme 1



**1** X = Cl
**2** X = I

not formed
**2′**

Scheme 2 When using MeLi obtained from MeCl, X = Cl; similarly, when MeI was used, X = I

Since two stereogenic centres (phosphorus and molybdenum) are present in complex **1**, two diastereoisomers may be expected; however, only one isomer can be detected (NMR) and isolated. This result can be explained as a consequence of the considerable steric interactions of the bulky $Cr(CO)_5$ group with the unsubstituted cyclopentadienyl ligand.

The X-ray crystal structure analysis of **1**‡ (Fig. 1) confirms the hitherto unknown capability of the $[(\eta^5\text{-}C_5H_4)PPh\{Cr(CO)_5\}C_6H_4]$ fragment to behave as a chelating ligand, that is to form both cyclopentadienyl–P and Mo–C bonds.

This structure shows a non-planar heterocyclic ring [Mo, C(7), P, C(5), C(6)] with a 2.202(6) Å Mo–C(6) bond comparable with that observed [2.192(4) Å] for Mo–C ($sp^2$) in $[(C_5H_5)Mo\{C_5H_4C(SCH{=}CHCN)SC(R){=}CR\}]$.[4] The Cr–P distance of 2.369(2) Å is slightly longer than in dibridged bimetallic complexes {2.284(3) Å in $[(\eta^5\text{-}C_5H_5)_2Ta(\mu\text{-}H)(\mu\text{-}PPh_2)Cr(CO)_5]$} but smaller than in μ-phosphido complexes {2.549(3) Å in $[(\eta^5\text{-}C_5H_5)_2Nb\{P(OMe)_3\}\{PPh_2Cr(CO)_5\}]$}.[5]

This reaction is quite reproducible, but is dependent on the method used to obtain the metallophosphide salt. When MeI is used to prepare the organolithium reagent instead of MeCl, the two diastereoisomeric complexes incorporating an iodine atom, **2** and **2′**, are present in the crude material (95 : 5) and can be

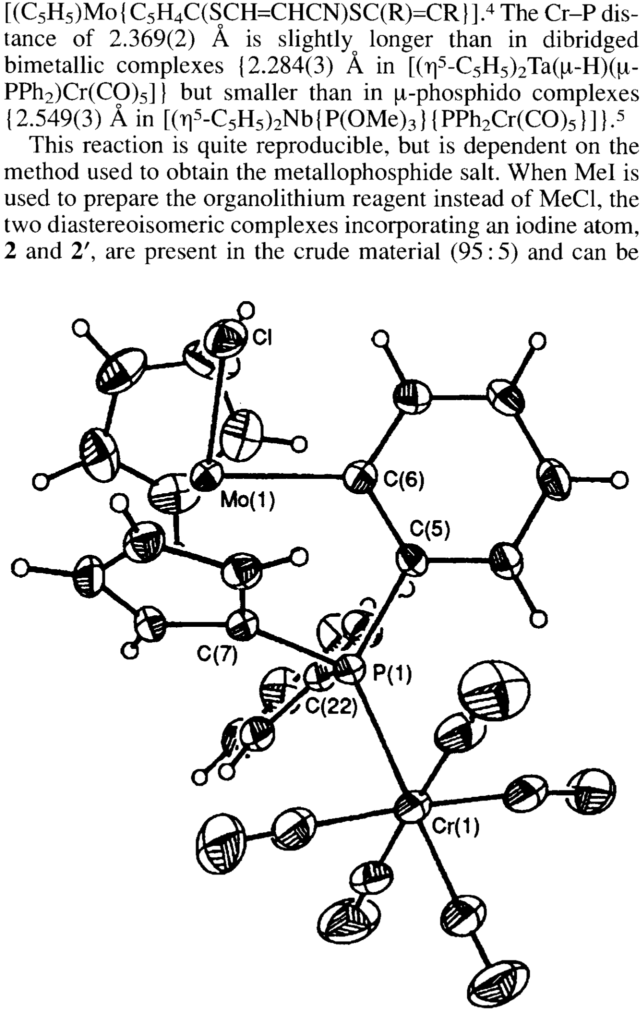


**Fig. 1** Crystal structure of **1**. Solvent molecule is omitted. Selected bond lengths (Å) and angles(°): Mo–Cl 2.476(2), Mo–C(6) 2.202(6), Cr–P 2.369(2), P–C(5) 1.817(6), P–C(22) 1.821(7), P–C(7) 1.809(6), Cl–Mo–C(6) 84.2(2), C(7)–P–Cr 114.2(2), C(7)–P–C(5) 95.2(3), C(5)–P–C(22) 103.8(3), C(7)–P–C(22) 103.4(3).

isolated after chromatographic work-up. These compounds are analytically and spectroscopically characterized; and exhibit almost identical spectra, except that the unsubstituted cyclopentadienyl proton resonance is *ca.* 0.7 ppm more shielded in **2**; the 'beam effect' of the (unsubstituted)phenyl anisotropy is the cause of the chemical shift difference of the two diastereoisomers.

From a mechanistic point of view, formation of these complexes can result from the following sequence: (*i*), nucleophilic *exo*-addition of the metallophosphide anion to one of the cyclopentadienyl rings[6,8] or direct nucleophilic substitution at molybdenum;[7,8] (*ii*) subsequent internal rearrangement with hydrogen migration to the metal centre leading to a cyclopentadienyl-substituted intermediate; (*iii*) reductive elimination of HCl to give the reactive 'molybdocene' species; (*iv*) insertion into the C–H bond of the phenyl group followed by an H/Cl (or I) exchange.[8]

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## Footnotes

† *Spectral data* for **1**: $^1H$ NMR (200 MHz, $CDCl_3$) δ 4.10 (1H, m, $C_5H_4$), 4.65 (5H, s, $C_5H_5$), 5.13 (1H, m, $C_5H_4$), 5.67 (1H, m, $C_5H_4$), 5.93 (1H, m, $C_5H_4$), 7.07–8.06 (9H, m, $C_6H_5$ and $C_6H_4$); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) δ 63.2; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 91.1 ($C_5H_4$), 97.7 ($C_5H_5$), 97.9 ($C_5H_4$), 101.8 ($C_5H_4$), 102.9 ($C_5H_4$), 116.5 ($C_5H_4$), 124.3, 129.3, 129.7, 130.4, 131.1, 133.9, 136.0, 145.9, 157.4, 170.7 (aryl-C), 217.1 (4CO), 221.8 (CO); FD-MS ($CHCl_3$) *m*/*z* 638.0 [$M^+$]. **2** $^1H$ NMR (200 MHz, $CDCl_3$) δ 4.36 (1H, m, $C_5H_4$), 4.67 (5H, s, $C_5H_5$), 5.05 (1H, m, $C_5H_4$), 5.22 (1H, m, $C_5H_4$), 6.44 (1H, m, $C_5H_4$), 7.07–8.55 (9H, m, $C_6H_5$ and $C_6H_4$); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) δ 61.9; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 91.8 ($C_5H_4$), 94.3 ($C_5H_4$), 95.4 ($C_5H_5$), 97.5 ($C_5H_4$), 101.6 ($C_5H_4$), 111.7 ($C_5H_4$), 124.1, 129.3, 129.6, 130.6, 131.0, 134.1, 136.2, 151.2, 157.4, 169.4 (aryl-C), 217.1 (4CO), 221.7 (CO), FD-MS ($CHCl_3$) *m*/*z* 730.1 [$M^+$]; **2′** $^1H$ NMR (200 MHz, $CDCl_3$) δ 4.9 (1H, m, $C_5H_4$), 5.27 (2H, m, $C_5H_4$), 5.38 (5H, s, $C_5H_5$), 6.32 (1H, m, $C_5H_4$), 7.03–8.43 (9H, m, $C_6H_5$ and $C_6H_4$); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) δ 49.2; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 94.8 ($C_5H_4$), 95.3 ($C_5H_4$), 95.7 ($C_5H_5$), 99.2 ($C_5H_4$), 103.4 ($C_5H_4$), 110.6 ($C_5H_4$), 124.1, 128.8, 129.2, 130.2, 130.5, 132.1, 141.0, 150.9, 160.8, 161.0 (aryl-C), 217.2 (4CO), 220.8 (CO), FD-MS ($CHCl_3$) *m*/*z* 730.1 [$M^+$].

‡ *Crystal data* for **1**: black crystals of **1** were grown with one solvent molecule ($CH_2Cl_2$) per formula unit; $C_{27}H_{18}ClCrMoO_5P$, $M = 637.9$, monoclinic, space group $P2_1/a$; $a = 16.028(8)$, $b = 10.739(6)$, $c = 16.220(9)$ Å, $\beta = 90.84(4)°$; $V = 2791.6$ Å$^3$, $Z = 4$, $D_c = 1.72$ g cm$^{-3}$; λ (Mo-Kα) = 0.71073 Å; 5828 reflections measured, 3930 independent [$I > 2.5\sigma(I)$]. Lorentz–polarization correction ($\mu = 12.0$ cm$^{-1}$). The structure was solved and refined by conventional three-dimensional Patterson, difference Fourier and full-matrix least-squares methods. All non-hydrogen atoms were refined with anisotropic temperature factors. All hydrogen atoms were placed in calculated positions riding on the carbon atoms bearing them and included in the final calculations, all H atoms had a fixed $U = 0.08$. $R = 0.055$, $R_w = 0.052$; GOF = 2.75; residual electron density 1.36/−1.22 e Å$^{-3}$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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