

MeO-Biphep as an Eight-Electron Donor to Ruthenium(II). Chiral Dialkyl Complexes with an Unprecedented Binding Mode

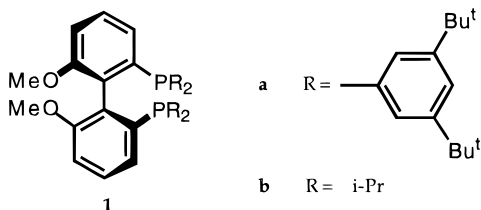
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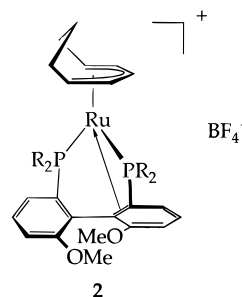
Summary: The chiral bis(3,5-di-*tert*-butylphenyl)phosphino MeO-Biphep complex $Ru(OAc)_2(\mathbf{1a})$, with two complexed *P* donors, reacts with MeLi to give $Ru(Me)_2(\mathbf{1a})$, in which only one *P* atom is coordinated together with an arene η^6 - C_6H_3 moiety derived from one of the biaryl rings. This is an unprecedented binding mode for this type of chiral complex.

Chiral bidentate phosphines are amongst the most important auxiliaries in enantioselective homogeneous catalysis.¹ Within this group, the atropisomeric compounds (e.g., the Binap² and Biphep³ classes) have been widely employed with impressive success, especially in the hydrogenation chemistry associated with Ru(II).^{2–4} We have recently shown⁵ that the chiral MeO-Biphep (ligands **1**) afford the novel pentadienyl cationic com-

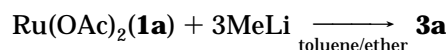


plexes $Ru(\eta^5-C_5H_5)(\mathbf{1})^+(\mathbf{2})$, in which these bidentate ligands function as *six*-electron donors, with the two additional electrons arising from the coordination of a biaryl double bond. This is an unexpected coordination mode and allows this ligand class additional electronic flexibility.

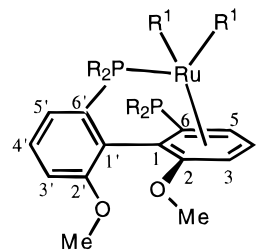
We show here that the same ligand can distort even further, by *dissociating* one of the two *P* atoms and complexing one of the ligand biaryl moieties; i.e., a 1,2,6-trisubstituted η^6 -arene compound is formed. Ligand **1a** now functions as an *eight*-electron donor, in which only a single tertiary phosphine atom is coordinated to ruthenium.



Reaction of $Ru(OAc)_2(\mathbf{1a})$ with 3 equiv of methyl-lithium affords the dimethyl complex $RuMe_2(\mathbf{1a})$ (**3a**) in good yield.⁶ The ³¹P NMR spectrum of **3a** reveals



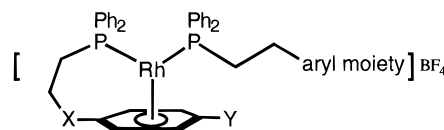
two widely separated resonances, δ 65.8 and -17.5 ppm (!), with the latter appearing at even lower frequency than the uncomplexed ligand, (δ -12.7 ppm). The observed $J(P,P)$ value of ca. 4 Hz (see Figure 1) is much too small for two nonequivalent ³¹P spins to both be coordinated to Ru. In addition to the two nonequivalent ¹³C methyl resonances, (δ -5.3 and -8.7 ppm), the ¹H and ¹³C spectra show three aryl resonances shifted to unexpectedly low frequency (see the C,H correlation in Figure 2). These three CH biaryl ¹³C signals appear between 70 and 100 ppm, in agreement with the literature for π -arene complexes.⁷ Together with the mass spectral and microanalytical data, these NMR data⁸ indicate that the complex has the structure



3a: $R^1 = CH_3$, $R = 3,5$ -di-*tert*-butylphenyl

3b: $R^1 = CH_2Si(CH_3)_3$, $R = 3,5$ -di-*tert*-butylphenyl

There are examples of phosphine–arene donors in the literature,⁹ however, these are of a more conventional type⁹



in which arene complexation is preplanned via the use

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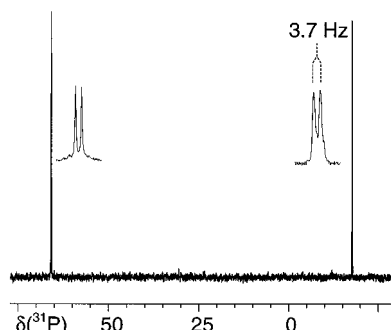


Figure 1. ^{31}P NMR spectrum for **3a**. Note (a) the low-frequency position of the uncomplexed P donor and (b) the very small $J(\text{P},\text{P})$ value (162 MHz, CD_2Cl_2).

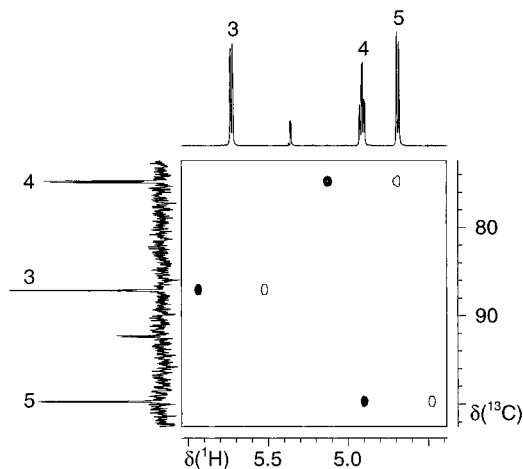


Figure 2. Section of the phase-sensitive HMQC, ^1H -detected ^{13}C , ^1H correlation for **3a** showing the relatively low frequency positions of the three biaryl CH resonances, indicated as C3–C5, from the coordinated η^6 -biaryl ring. The three remaining resonances appear at 102.9 (C1), 134.2 (C2, carrying the OMe group), and 92.3 (C6) ppm, respectively, with the last signal visible in the section shown. The open and closed cross-peaks reflect the phases; the horizontal and vertical 1-D spectra are shown for clarity. The unlabeled signal in the proton direction arises from CH_2Cl_2 (^{13}C at 100.6 MHz, ^1H at 400 MHz, CD_2Cl_2).

of spacer methylene groups. Moreover, these compounds are not involved in enantioselective hydrogenation.

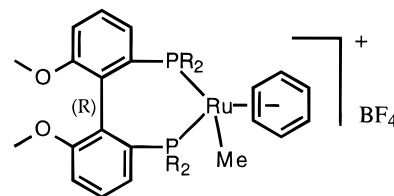
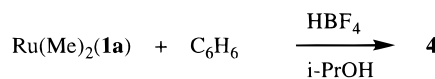
A related reaction using ((trimethylsilyl)methyl)-lithium gave **3b**, and apart from the (trimethylsilyl)-methyl ligands, the NMR spectroscopic details¹⁰ for this analog are similar to those for **3a**. Both **3a** and **3b** are stable 18e complexes of Ru(II) containing an unprecedented coordination mode for the chiral MeO-Biphep

(6) Synthesis of $\text{Ru}(\text{Me})_2(\mathbf{1})$ (**3a**): To a solution of 57.2 mg (0.004 57 mmol) of $\text{Ru}((R)\text{-}(3,5\text{-}t\text{-Bu})_2\text{-MeO-BIPHEP})(\text{OAc})_2$ in 2 mL of toluene was added 3 equiv of methylolithium (1.6 M solution in diethyl ether; 85 μL , 0.14 mmol). After 1 h the orange solution was stirred for ca. 15 s in air before it was evaporated to dryness. The residue was extracted with 2×3 mL of hexane. After filtration of the extracts through Celite, the pale yellow solution was evaporated to dryness, to afford 48.4 mg (91%) of a yellow powder. Anal. Calcd for $\text{C}_{72}\text{H}_{102}\text{O}_2\text{P}_2\text{Ru}$: C, 74.38; H, 8.84. Found: C, 74.16; H, 8.73. IR (CsI): 595, 483 cm^{-1} . MS (FAB): m/z 1148.5 ($[\text{M} - \text{Me}]^+$), 1132.4 ($[\text{M} - 2\text{Me}]^{2+}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ = 65.8, -17.5 ppm [$J(\text{P},\text{P})$ = 3.7 Hz]. ^1H (^{13}C) NMR: δ Me, 0.10 (-8.7); Me, -0.48 (-5.3); for the complexed biaryl positions 1–6, respectively (102.9), (134.2), 5.69 (87.1), 4.87 (74.8), 4.65 (99.9), (92.3); for the normal biaryl positions 1'–6' (133.2), (158.7), 6.60 (109.7), 7.28 (129.7), 6.80 (124.8), (123.1); MeO, 2.79 (53.9), 3.58 (59.7); *ortho* H for the 3,5-di-*tert*-butylphenyl groups, 6.63, 6.84, 7.15, 7.30; *t*-Bu 1.05, 1.24, 1.32, 1.35. There are five resolved ^{13}C *t*-Bu methyl signals between 31.5 and 31.8 ppm, in the ratio 1:1:2:2:2.

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chelate. Compounds **3a,b** are also the first reported stable Ru(II) dialkyl complexes containing a chiral auxiliary.

The methyl complex **3a** reacts smoothly, in high yield, with 1, or even 2 equiv of HBF_4 in the presence of excess benzene to yield the somewhat more conventional 18e monomethyl $\eta^6\text{-C}_6\text{H}_6$ derivative **4**, in which both phosphorus donors are again coordinated.¹¹ Obviously, if given a choice, the metal favors the classical mode of arene coordination, which is presumably less strained.



4: R = 3,5-di-*tert*-butylphenyl

It is interesting that **1a** can readily take up so many novel coordination modes, and studies relating these new complexes to catalytic reactions are in progress.

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(8) The NMR assignments were made on the basis of COSY, NOESY, P,H, C,H (both one-bond and long-range HMBC two- and three-bond) 2-D correlations. The P,H correlations are important in that they pinpoint the various *ortho* aromatic protons, which are useful NOE probes. The aromatic protons of the 3,5-di-*tert*-butylphenyl groups show the usual $^3J(\text{P},\text{H})$ values of ca. 7–8 Hz. The $J(\text{P},\text{H})$ values to the complexed arene are much smaller, presumably due to the complexation. The resolutions in the ^1H and ^{13}C spectra are ± 0.3 and ± 0.6 Hz, respectively.

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(10) Synthesis of $\text{Ru}(\text{trimethylsilyl)methyl}\{(\text{R})\text{-}(\mathbf{1a})\}$ (**3b**): To a solution of 48.0 mg (0.003 83 mmol) of $\text{Ru}((R)\text{-}(\mathbf{1a}))(\text{OAc})_2$ in 2 mL of toluene was added 3.9 equiv of $\text{Me}_3\text{SiCH}_2\text{Li}$ (150 μL , 0.150 mmol of a 1.0 M solution in pentane). After 24 h the orange solution was taken to dryness. The residue was redissolved in 2 mL of CH_2Cl_2 and stirred for another 24 h. After evaporation to dryness, 2 mL of hexane was added. This mixture was then transferred into an NMR tube and stored for 1 day at -30 $^\circ\text{C}$ in order to let the lithium salts precipitate. After decantation and evaporation to dryness 38.1 mg (76%) of a yellow powder was isolated. MS (FAB): m/z 1250.6 ($[\text{M} - \text{tert-butyl}]^+$), 1234 ($[\text{M} - \text{SiMe}_3]^+$). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 60.8, -18.4 [$J(\text{P},\text{P})$ = 6 Hz]. ^1H (^{13}C) NMR: δ first CH_2SiMe_3 , -0.63 (-7.05), 1 H, $^2J(\text{H},\text{H})$ = 13.3 Hz, $^3J(\text{P},\text{H})$ = 13.2 Hz; -0.81 (-7.05), 1 H, $^2J(\text{H},\text{H})$ = 13.3 Hz, $^3J(\text{P},\text{H})$ = 3.5 Hz; second CH_2SiMe_3 , -0.70 (-5.82), 2 H, tightly coupled AB spin system, $^3J(\text{H},\text{H})$ = ca. 14–15 Hz, $^3J(\text{P},\text{H})$ = 7.0 Hz; 2 SiMe₃, -0.23 (3.56), 9H, -0.50 (3.92), 9H; complexed biaryl positions 1–6, respectively (103.6), (132.3), 6.15 (88.0), 5.32 (71.5), 5.33 (94.6), (91.4); normal biaryl 1'–6', (134.0), (158.3), 6.66 (110.0), 7.34 (129.5), 6.80 (126.6), C6' not assigned; MeO, 2.94 (54.2), 3.59(62.2); *ortho* H for the 3,5-di-*tert*-butylphenyl, 6.88, 7.15 (two sets of two which overlap), 7.61; *t*-Bu, 1.11, 1.19, 1.34, 1.43.

(11) Synthesis of $[\text{Ru}(\text{Me})((R)\text{-}(\mathbf{1a}))(\text{benzene})]\text{BF}_4$ (**4**): To a solution of $\text{Ru}(\text{Me})_2((R)\text{-}(\mathbf{1a}))$, (**3a**; 34.0 mg, 0.0292 mmol) in 2 mL of *t*-PrOH was added 20 μL of benzene, followed by the addition of 2 equiv of $\text{HBF}_4 \cdot \text{H}_2\text{O}$ (c 8.2 M; 2.0 equiv, 7.2 μL , 0.058 mmol). The reaction mixture was refluxed shortly and then stirred for 3 h at room temperature. Subsequently, the solvent was distilled, (in vacuo) and the crude product redissolved in 4 mL of CH_2Cl_2 . This solution was dried over MgSO_4 . Evaporation to dryness gave 35.7 mg (93%) of a yellow powder. Anal. Calcd for $\text{C}_{77}\text{H}_{105}\text{BF}_4\text{O}_2\text{P}_2\text{Ru}$: C, 70.46; H, 8.06. Found: C, 69.48; H, 7.62. MS (FAB): m/z 1225.7 ($[\text{M}]^+$). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 46.5, 45.6 [$J(\text{P},\text{P})$ = 57 Hz]. ^1H (^{13}C) NMR: δ Me, 0.42 (-5.7), $^3J(\text{P},\text{H})$ = 6 Hz (both P atoms exhibit the same 3J value), $^2J(\text{P},\text{C})$ = 12.5 Hz; $\eta^6\text{C}_6\text{H}_6$, 5.28 (96.2), $^2J(\text{P},\text{C})$ = 2.4 Hz.