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Reaction of $[RuCl_2(DMSO)_4]$ with aromatic phosphines bearing *ortho*-methoxy groups †

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Reaction of $[RuCl_2(DMSO)_4]$ **1** with (2,6-dimethoxyphenyl)diphenylphosphine (MDMPP) in acetone–CH_2Cl_2 at reflux gave *t,c,c*-$[RuCl_2(MDMPP\text{-}\kappa^2P,O)_2]$ **2**. Reaction with bis(2,6-dimethoxyphenyl)phenylphosphine (BDMPP) afforded the phosphonium salt containing a ruthenium(II) anion, $[BDMPP(CH_2Cl)][RuCl_3(DMSO)_3]$ **3b**, $[BDMPP(CH_2Cl)][RuCl(DMSO)_2\{PPh(C_6H_3OMe\text{-}6\text{-}O\text{-}2)_2\text{-}\kappa^3P,O,O'\}]$ **4b** and $[BDMPP(CH_3)][RuCl(DMSO)_2\{PPh(C_6H_3OMe\text{-}6\text{-}O\text{-}2)_2\text{-}\kappa^3P,O,O'\}]$ **4d** [$BDMPP(CH_2Cl) = \{2,6\text{-}(MeO)_2C_2H_3\}_2PhP(CH_2Cl)$, $BDMPP(CH_3) = \{2,6\text{-}(MeO)_2C_6H_3\}_2PhP(CH_3)$]; complexes **4** contain tridentate P,O,O′ co-ordination in which two methoxy groups of BDMPP were demethylated. These structures were confirmed by X-ray analyses. Tris(2,6-dimethoxyphenyl)phosphine (TDMPP) reacted with **1** to give **3c** $[TDMPP(CH_2Cl)][RuCl_3(DMSO)_3]$ [$TDMPP(CH_2Cl) = \{2,6\text{-}(MeO)_2 C_6H_3\}_3P(CH_2Cl)$]. Complex **2** reacted with xylyl or mesityl isocyanide to give *mer*-$[RuCl_2(MDMPP\text{-}P)(RNC)_3]$ **5**. Reaction with CO afforded $[RuCl_2(MDMPP\text{-}P)(MDMPP\text{-}\kappa^2P,O)(CO)]$ **6** and an insoluble unidentified complex. The structure of **6** was confirmed by an X-ray analysis; one MDMPP group acts as a P,O bidentate ligand, the other as a monodentate ligand, and a CO ligand occupies the *trans* position to an oxygen atom. Two Cl and two P atoms were located at mutually *trans* positions. The phosphonium salt $[BDMPP(CH_2Cl)]Cl$, derived from CH_2Cl_2 and BDMPP, reacted with **1** to afford **3b**. The reaction of **3b** with BDMPP gave **4b** and **4d**. The reaction pathways are discussed.

Tris(2,4,6-trimethoxyphenyl)phosphine (TMPP) bearing methoxy groups at the 2,4 and 6 positions of the phenyl groups exhibits high basicity and nucleophilicity.[1–3] The transition metal chemistry of this phosphine has been studied by Dunbar's group.[4] It can act as a mono-, bi- and tri-dentate ligand. The reaction of a square-planar complex $[Pd(NCCH_3)_4][BF_4]_2$ with TMPP gave a pseudo-octahedral complex $[Pd(TMPP\text{-}\kappa^3P,O,O')_2][BF_4]_2$ defined by two phosphorus and two ether-oxygen atoms in an equatorial arrangement, and two ether-oxygen atoms in axial sites.[5a] The reaction of the six-co-ordinate complex $[Ni(NCCH_3)_6][BF_4]_2$ and TMPP gave a square-planar complex *cis*$[Ni(TMPP\text{-}\kappa^2P,O)_2]$ in which the metal atom is surrounded by two phosphorus atoms and two phenoxide-O atoms.[6] Recently, palladium and platinum analogs of the four-co-ordinate nickel complex have been isolated.[5b]

We have been interested in the reactions of aromatic phosphines bearing methoxy groups at 2,6 positions with transition metal complexes. Aromatic phosphines such as (2,6-dimethoxyphenyl)diphenylphosphine (MDMPP), bis(2,6-dimethoxyphenyl)phenylphosphine (BDMPP), and tris(2,6-dimethoxyphenyl)phosphine (TDMPP) show a variety of reactivity similar to that of TMPP. We have reported that reactions of bis[(η^6-arene)dichlororuthenium(II)] or bis[dichloro(η^5-pentamethylcyclopentadienyl)rhodium(III)] with MDMPP, BDMPP or TDMPP gave various types of complexes bearing a *P*, ether-*O* [(κ^2P,O) or (κ^3P,O,O')] and phenoxide-O co-ordination [(κ^2P,O) or (κ^3P,O,O')], depending on the complexes, phosphines and reaction conditions.[7,8]

Transition-metal complexes of dimethyl sulfoxide (DMSO) are useful starting materials for many inorganic and organometallic compounds.[9] Recently we have reported that $[RuCl_2(DMSO)_4]$ in the presence of $Na_2(xdk)_4\cdot H_2O$ [H_2xdk = *m*-xylenediamine bis(Kemp's triacid imide)][10] gave $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)(\mu\text{-}DMSO\text{-}S,O)Cl_2(DMSO\text{-}S)_4]$ in which one DMSO acts as a S,O-bidentate ligand.[11] We have been interested in reactivities of the aforementioned bulky phosphines having high basicity towards octahedral metal complexes in relation with the difference in co-ordination numbers found in acetonitrile complexes of palladium and nickel.[5a,6] We found that the octahedral complex $[RuCl_2(DMSO)_4]$ **1** reacted readily with these phosphines in CH_2Cl_2 to generate the $[RuCl_3(DMSO\text{-}S)_3]^-$ anion as the phosphonium salt. This reaction provides a method to convert neutral complexes into anionic ones.

Experimental

All reactions were carried out under a nitrogen atmosphere. Complex **1**,[12] phosphines (MDMPP, BDMPP and TDMPP),[1] isocyanides[13] and phosphonium salts[1b] ($[BDMPP(CH_2Cl)]Cl$, $[BDMPP(CH_3)]Cl$, and $[TDMPP(CH_2Cl)]Cl$) were prepared according to the literature methods. Dichloromethane was distilled from CaH_2 and diethyl ether from $LiAlH_4$. Other reagents were available commercially. The infrared and electronic absorption spectra were measured on FT/IR-5300 and U-best 30 spectrometers, respectively, ^1H (250 MHz) and $^{31}P\text{-}\{^1H\}$ NMR spectra using 85% H_3PO_4 as external reference on a Bruker AC250, and fast atom bombardment (FAB) mass spectra on a JMS-DX300 spectrometer.

Reactions of complex 1

With MDMPP. A mixture of complex **1** (72 mg, 0.15 mmol) and MDMPP (208 mg, 0.65 mmol) was refluxed in acetone–CH_2Cl_2 (1 : 1 ratio, 40 mL). After 1.5 h the solvent was removed to *ca.* 5 ml and diethyl ether added to form reddish violet crystals of *t,c,c*-$[RuCl_2(MDMPP\text{-}\kappa^2P,O)_2]$ **2** (31.4 mg, 26%), which were identified by comparison with spectroscopic data of an authentic sample.[7]

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† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. see http://www.rsc.org/suppdata/dt/1999/4003/

With BDMPP. A mixture of complex **1** (72 mg, 0.15 mmol) and BDMPP (85 mg, 0.22 mmol) was stirred in CH_2Cl_2 (20 mL) at room temperature. After 4 h the solvent was removed and the residue recrystallized from CH_2Cl_2 and diethyl ether to give yellow crystals of [BDMPP(CH_2Cl)][*fac*-$RuCl_3$(DMSO-*S*)$_3$] **3b** (87 mg, 67%). The further recrystallization of the mother-liquor gave white crystals of [BDMPP(CH_2Cl)][RuCl(DMSO-*S*)$_2${PPh(C_6H_3OMe-6-O-2)$_2$-κ^3*P*,*O*,*O*′}] **4b** (15.3 mg, 10%) and [BDMPP(CH_3)][RuCl(DMSO-*S*)$_2${PPh(C_6H_3OMe-6-O-2)$_2$-κ^3*P*,*O*,*O*′}] **4d** (2 mg) [BDMPP(CH_3) = PPh{2,6-(MeO)$_2$-C_6H_3}$_2$(Me)]. Complex **3b**: FAB MS *m*/*z* 431 (M^+ of a cation); ^{1}H NMR($CDCl_3$) δ 3.54 (s, DMSO, 18 H), 3.62 (s, OMe, 12 H), 4.86 (d, J_{PH} = 6.3 Hz, CH_2, 2 H) and 6.75–7.80 (m, Ph, 22 H); ^{31}P-{^{1}H} NMR($CDCl_3$) δ 14.92 (s) (Calc. for $C_{29}H_{43}Cl_4O_7PRuS_3$: C, 39.86; H, 4.96; Cl, 16.23; S, 11.01. Found: C, 39.06; H, 4.73; Cl, 15.49; S, 11.30%). Complex **4b**: FAB MS: *m*/*z* 431 (M^+ of a cation); ^{1}H NMR($CDCl_3$) δ 2.56 (s, MeS, 3 H), 2.72 (s, MeS, 3 H), 2.96 (s, MeS, 3 H), 3.26 (s, MeS, 3 H), 3.41 (s, MeO, 3 H in an anionic species), 3.48 (s, MeO, 3 H in an anionic species), 3.58 (s, MeO in a cationic species, 12 H), 4.89 (d, J_{PH} = 6.5 Hz, PCH_2, 2 H) and 5.85–7.80 (m, Ph, 22 H); ^{31}P-{^{1}H} NMR($CDCl_3$) δ 14.96 (s, phosphonium, 1P) and 67.8 (s). Complex **4d**: ^{1}H NMR($CDCl_3$) δ 2.56 (s, MeS, 3 H), 2.72 (s, MeS, 3 H), 2.96 (s, MeS, 3 H), 3.26 (s, MeS, 3 H), 3.41 (s, MeO, 3 H), 3.48 (s, MeO, 12 H), 2.58 (d, J_{PH} = 14.2 Hz, PMe, 3 H), 3.57 (s, MeO in a phosphonium species, 12 H), 5.27 (s, CH_2Cl $_2$) and 5.75–7.80 (m, Ph, 22 H); ^{31}P-{^{1}H} NMR($CDCl_3$) δ 8.64 (s, phosphonium, 1P) and 67.8 (s, an anion, 1P) (Calc. for $C_{49}H_{61}ClO_{10}P_2RuS_2\cdot1.5CH_2Cl_2$: C, 50.54; H, 5.37. Found: C, 50.82; H, 5.38%).

With TDMPP. A mixture of complex **1** (73 mg, 0.15 mmol) and TDMPP (151 mg, 0.34 mmol) was stirred in CH_2Cl_2 (10 mL) at room temperature. After 1.5 h the work-up of the reaction mixture and recrystallization from CH_2Cl_2 and diethyl ether gave yellow crystals of [TDMPP(CH_2Cl)][*fac*-$RuCl_3$-(DMSO-*S*)$_3$] **3c** (69 mg, 71%). FAB MS *m*/*z* 491 (M^+ of a cation). ^{1}H NMR($CDCl_3$) δ 3.55 (s, DMSO, 18 H), 3.60 (s, OMe, 18 H), 4.86 (d, J_{PH} = 7.0 Hz, CH_2, 2 H), 6.6 (m, *m*-H, 6 H) and 7.56 (t, *p*-H, 3 H). ^{31}P-{^{1}H} NMR($CDCl_3$) δ 9.99 (s). Calc. for $C_{31}H_{47}Cl_4O_9PRuS_3$: C, 39.87; H, 5.07. Found: C, 39.46; H, 4.97%.

With [TDMPP(CH_2Cl)]Cl. A mixture of complex **1** (144.3 mg, 0.30 mmol) and phosphonium salt **5c** (292.4 mg, 0.59 mmol) was stirred in CH_2Cl_2 at room temperature. After 3 h the solution was concentrated to *ca.* 3 mL and diethyl ether added to yield yellow crystals of **3c** (220 mg, 79%). Compound **3b** was prepared from **1** and [BDMPP(CH_2Cl)]Cl in a similar manner.

Reaction of complex 3b with BDMPP

A mixture of complex **3b** (50.6 mg, 0.06 mmol) and BDMPP (100 mg, 0.26 mmol) was refluxed in MeOH (20 mL) for 3 h. The solution was concentrated to *ca.* 3 mL and diethyl ether added to give white crystals of **4d** (33.3 mg, 53.6%) and a small amount of **4b**.

Reactions of complex 2

With 2,6-Xylyl isocyanide (XylNC). A mixture of complex **2** (73 mg, 0.089 mmol) and XylNC (42 mg, 0.32 mmol) was stirred in CH_2Cl_2 (20 mL) at room temperature. After 6 h the solvent was removed to *ca.* 5 mL and diethyl ether added to form yellow crystals of *mer*-[$RuCl_2$(MDMPP-*P*)(XylNC)$_3$] **5a** (39 mg, 49%). IR(Nujol): 2168 and 2110 cm^{-1} (N≡C). UV-vis(CH_2Cl_2) λ_{max} 324 nm. ^{1}H NMR($CDCl_3$) δ 2.30 (s, *o*-Me, 12 H), 2.54 (s, *o*-Me, 6 H), 3.05 (s, OMe, 6 H) and 6.43–8.23 (m, Ph, 22 H). ^{31}P-{^{1}H} NMR($CDCl_3$) δ 21.40 (s). Calc. for $C_{47}H_{46}Cl_2N_3O_2PRu$: C, 63.58; H, 5.22; N, 4.73. Found: C, 63.62; H, 5.16; N, 4.78%.

According to the above procedures, the mesityl isocyanide complex, *mer*-[$RuCl_2$ (MDMPP-*P*)(MesNC)$_3$] **5b** (45%) was obtained from the reaction of **2** with mesityl isocyanide (MesNC). IR(Nujol) 2170 and 2110 cm^{-1} N(≡C). UV-vis(CH_2Cl_2) λ_{max} 324 nm. ^{1}H NMR($CDCl_3$) δ 2.23 (s, *o*-Me, 18 H), 2.24 (s, *p*-Me, 3 H), 2.48 (s, *p*-Me, 3 H), 3.06 (s, OMe, 6 H) and 6.43–8.22 (m, Ph, 19 H). ^{31}P-{^{1}H} NMR($CDCl_3$) δ 21.83 (s). Calc. for $C_{50}H_{52}Cl_2N_3O_2PRu$: C, 64.58; H, 5.64; N, 4.52. Found: C, 64.28; H, 5.56; N, 4.34%.

With CO. Into a solution of complex **2** (72 mg, 0.088 mmol) in CH_2Cl_2 (35 mL) was bubbled carbon monoxide for 5 min at room temperature. After 5.5 h the resulting white precipitate (74.7 mg) was filtered off, and the filtrate concentrated to *ca.* 5 mL. Diethyl ether was added to give yellow crystals of [$RuCl_2$(MDMPP-*P*)(MDMPP-κ^2*P*,*O*)(CO)] **6** (4 mg, 6%). FAB MS: *m*/*z* 844 (M^+) and 816 (M − CO^+). IR(Nujol) 1962 cm^{-1} (C≡O). ^{1}H NMR (CD_2Cl_2) δ 3.53 (s, MeO, 12 H) and 6.6–8.1 (c, Ph, 23 H). ^{31}P-{^{1}H} NMR(CD_2Cl_2) δ 30.31 (br s, 1P). White solid: IR(Nujol) 2010 and 1983 cm^{-1} (C≡O). Constant values were not obtained in the elemental analysis.

Crystallography

Complexes **3b**, **4b**, **5a**, **5b** and **6** were recrystallized from CH_2Cl_2–diethyl ether. The crystal parameters along with data collection are summarized in Table 1. Data intensities were measured by the 2θ–ω scan method using graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å) at 27° and corrected for Lorentz-polarization effects. No decay was observed. Absorption corrections were made with empirical ψ scans. Atomic scattering factors were taken from Cromer and Waber.[14] Anomalous dispersion effects were included in F_{calc};[15] the values of $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[16] All calculations were performed using the TEXSAN crystallographic software package.[17]

All structures were solved by Patterson methods (DIRDIF 92)[18] and refined by full-matrix least-squares methods. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were calculated at the ideal positions with C–H distances of 0.95 Å.

CCDC reference number 186/1676.

See http://www.rsc.org/suppdata/dt/1999/4003/ for crystallographic files in .cif format.

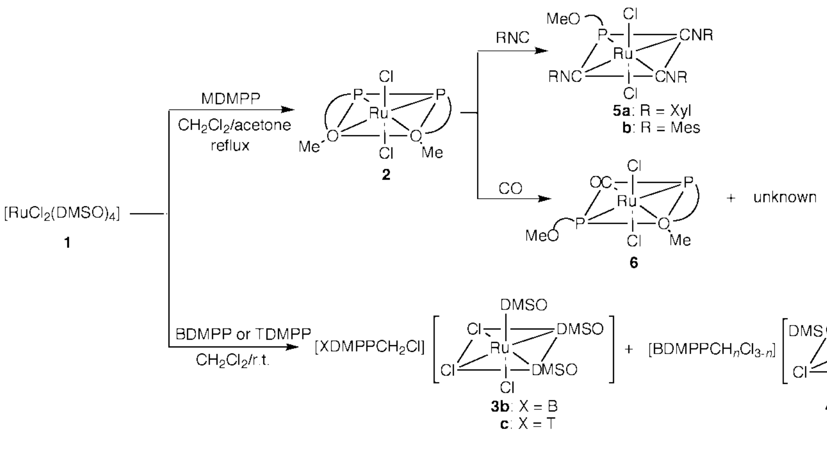
Results and discussion

Reactions in dichloromethane

When [$RuCl_2$(DMSO)$_4$] **1** was treated with four equivalents of MDMPP in CH_2Cl_2 **1** was recovered quantitatively, but the reaction in refluxing acetone–CH_2Cl_2 gave the known reddish violet compound *t*,*c*,*c*-[$RuCl_2$(MDMPP-κ^2*P*,*O*)$_2$] **2** (Scheme 1).[7] A similar reaction of **1** with BDMPP in a 1 : 2 molar ratio in CH_2Cl_2 at room temperature afforded a yellow compound (main product) formulated as [BDMPP(CH_2Cl_2)] [$RuCl_3$-(DMSO-*S*)$_3$] **3b** in addition to two white complexes (minor products), [BDMPP(CH_2Cl)][RuCl(DMSO-*S*)$_2${PPh(C_6H_3-OMe-6-O-2)$_2$-κ^3*P*,*O*,*O*′}] **4b** and [BDMPP(CH_3)] [RuCl-(DMSO-*S*)$_2${PPh(C_6H_3OMe-6-O-2)$_2$-κ^3*P*,*O*,*O*′)}] **4d**. The FAB mass spectroscopy of **3b** and **4b** showed the same molecular peak at *m*/*z* 431 which was consistent with the presence of [BDMPP(CH_2Cl)]$^+$. The ^{1}H NMR spectrum of **3b** showed two singlets at δ 3.54 and 3.62, and a doublet at δ 4.86, in a 18 : 12 : 2 intensity ratio, assignable to DMSO, methoxy and methylene groups, respectively. In the ^{31}P-{^{1}H} NMR spectrum only one peak appeared at δ 14.92. These spectroscopic data suggested a salt-like compound [BDMPP(CH_2Cl)][$RuCl_3$(DMSO-*S*)$_3$]. The stereochemistry was confirmed by an X-ray analysis (Fig. 1). A similar conversion into a metal complex anion has been noted in the reaction of iron(III) chloride with TMPP to afford

Table 1 Crystal data of [BDMPP(CH$_2$Cl)][*fac*-RuCl$_3$(DMSO-*S*)$_3$] **3b**, [BDMPPCH$_2$Cl)][RuCl(DMSO-*S*)$_2${PPh(C$_6$H$_3$OMe-6-O-2)$_2$-κ^3*P*,*O*,*O*′}] **4b**, [RuCl$_2$(MDMPP)(XylNC)$_3$] **5a**, [RuCl$_2$(MDMPP)(MesNC)$_3$] **5b** and [RuCl$_2$(MDMPP)(MDMPP-κ^2*P*,*O*)(CO)] **6**

	3b	4b	5a	5b	6
Formula	$C_{29}H_{43}Cl_4O_7PRuS_3$	$C_{48}H_{59}Cl_4O_{10}P_2RuS_2$	$C_{47}H_{46}Cl_2N_3O_2Ru$	$C_{50}H_{52}Cl_2N_3O_2PRu$	$C_{42}H_{40}Cl_4O_5P_2Ru$
M	873.69	1164.94	887.85	929.23	929.60
Space group	$P2_1$ (no. 4)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P2_1$ (no. 4)	$P\bar{1}$ (no. 2)
a/Å	13.824(3)	14.253(3)	11.441(5)	11.667(3)	13.70(1)
b/Å	9.671(3)	16.592(3)	19.851(3)	20.205(4)	14.555(9)
c/Å	15.292(2)	12.623(3)	19.068(3)	19.932(4)	12.346(7)
α/°		102.13(2)			101.25(5)
β/°	112.35(1)	110.07(2)	83.17(2)	93.17(2)	114.69(5)
γ/°		102.09(2)			68.35(5)
V/Å^3	1890.8(9)	2609(1)	4323(2)	4691(1)	2075(2)
Z	2	2	4	4	2
μ/cm^{-1}	9.46	7.01	5.64	5.23	7.55
R, R′ (reflections	0.037, 0.041 (for 2858)	0.051, 0.064 (for 4831)	0.048, 0.065 (for 2846)	0.053, 0.111 (for 4334)	0.073, 0.098 (for 5251)



Scheme 1 Reactions of complex **1** with MDMPP, BDMPP and TDMPP; POMe = MDMPP; OPO = PPh{(2-O-6-MeO)$_2$C$_6$H$_3$}$_2$.

unexpectedly the dinuclear iron(II) chloride anion [Fe$_2$Cl$_6$]$^{2-}$ as the phosphonium salt [{2,4,6-(MeO)$_3$C$_6$H$_2$}$_3$ PH]$^+$.[19]

The ^{1}H NMR spectrum of complex **4b** showed seven singlets at δ 2.56, 2.72, 2.96, 3.26, 3.41, 3.48 and 3.58, in a 1 : 1 : 1 : 1 : 1 : 1 : 4 intensity ratio, in the methyl region and a doublet at δ 4.89 due to a methylene group. The chemical shifts of the resonances at δ 3.58 and 4.89 were in good agreement with those found for [BDMPP(CH$_2$Cl)]$^+$. The two resonances at δ 3.41 and 3.48 were tentatively assigned to the methoxy groups and others to the DMSO ligands in the anionic species [RuCl(DMSO-*S*)$_2${PPh(C$_6$H$_3$OMe-6-O-2)$_2$-P,O,O′}]. Six methyl groups due to DMSO and the tridentate P,O,O′ ligand were inequivalent. The ^{31}P-{^{1}H} NMR spectrum showed two resonances at δ 14.96 and 67.8 (s); the former was again similar to that found for [BDMPP(CH$_2$Cl)]$^+$.

The ^{1}H NMR spectrum of the anionic species [RuCl(DMSO-*S*)$_2$PPh(C$_6$H$_3$OMe-6-O-2)$_2$-κ^2*P*,*O*,*O*′}] in **4d** was in good agreement with that found in **4b**, whereas the resonances of a cationic species appeared at δ 2.58 due to the CH$_3$(P) protons as a doublet and at δ 3.57 due to the methoxy groups as a singlet, being similar to those for [BDMPP(CH$_3$)]Cl. Formation of **4d** showed that cation exchange had occurred.

Compound **1** reacted readily with TDMPP in CH$_2$Cl$_2$ at room temperature to give only yellow crystals of [TDMPP-CH$_2$Cl][RuCl$_3$(DMSO)$_3$] **3c** in high yield. The FAB mass spectroscopy showed a molecular peak (*m*/*z* 491) of [TDMP-P(CH$_2$Cl)]$^+$. The ^{1}H NMR spectrum showed two singlets at δ 3.55 and 3.60 and a doublet at δ 4.86 in a 18 : 18 : 2 intensity ratio, assignable to the DMSO, methoxy and methylene protons, respectively.

In attempts to examine the possible routes for formation of complexes **3** and **4**, the reaction of **1** with [BDMPP(CH$_2$Cl)]Cl was carried out at room temperature. It gave the corresponding complex **3b** in relatively high yield. Complex **3b** reacted with an excess of BDMPP in MeOH to produce **4d** as the main product and **4b** as the minor one, suggesting the occurrence of cation exchange between [BDMPP(CH$_2$Cl)]$^+$ and [BDMPP(CH$_3$)]$^+$. These results can be explained as follows. The reaction starts with the formation of the phosphonium salt, derived from BDMPP and CH$_2$Cl$_2$, and subsequently leads to **3b** by a nucleophilic attack of a Cl anion on the ruthenium atom of **1**. Compound **3b** reacts with an excess of phosphine to liberate two CH$_3$Cl molecules and is finally converted into **4b**.

The formation of the phosphonium salt is assumed to be a driving force for these reactions, which do not occur in acetone. The reactions of TDMPP, BDMPP or MDMPP with CH$_2$Cl$_2$ are known to form the corresponding phosphonium salts, [XDMPP(CH$_2$Cl)]Cl (X = M, B or T). The half-lives increase in the order of TDMPP, BDMPP and MDMPP, being 57, *ca.* 750 and 3740 min at 23 °C, respectively.[20] Since the formation of the phosphonium salt of MDMPP is very slow, the replacement of DMSO with phosphine proceeded to give **2** before the formation of a phosphonium salt, but **3c** was isolated exclusively because of the easy formation of the phosphonium salt. For BDMPP the formation of the phosphonium salt and the conversion of the resulting **3b** into **4b** are considered to occur concomitantly.

Reactions of complex 2

When complex **2** was treated with XylNC or MesNC in refluxing CH$_2$Cl$_2$, yellow crystals formulated as [RuCl$_2$(MDMP-P)(RNC)$_3$] (R = Xyl; **5a** or Mes **5b**) were isolated (Scheme 1). The IR spectra of **5** showed two bands at *ca.* 2170 and 2110 cm^{-1} due to the terminal isocyanide groups. The ^{1}H NMR spectra showed resonances due to two kinds of isocyanide groups in a 1 : 2 intensity ratio. These spectroscopic data suggested a meridional structure. The X-ray studies were in agreement with the proposed structure (Figs. 3 and 4).

Table 2 Selected bond lengths (Å) and angles (°) of [BDPMPP(CH$_2$Cl)][RuCl$_3$(DMSO-*S*)$_3$] **3b** and [BDPMPP(CH$_2$Cl)][RuCl(DMSO)$_2$-{PPh(C$_6$H$_3$OMe-6-O-2)$_2$-κ^3*P*,*O*,*O*′}] **4b**

Compound **3b**							
Ru–Cl(2)	2.420(2)	Ru–Cl(3)	2.438(2)	Ru–Cl(4)	2.435(2)		
Ru–S(1)	2.276(2)	Ru–S(2)	2.268(2)	Ru–S(3)	2.263(2)		
S(1)–O(5)	1.452(6)	S(2)–O(6)	1.472(5)	S(3)–O(7)	1.481(5)		
P–C(1)	1.811(7)	P–C(7)	1.795(7)	P–C(15)	1.800(7)		
P–C(23)	1.829(6)						
Cl(2)–Ru–Cl(3)	86.41(6)	Cl(2)–Ru–Cl(4)	88.43(7)	S(1)–Ru–S(2)	96.03(7)	S(1)–Ru–S(3)	92.67(7)
Cl(2)–Ru–S(1)	173.66(7)	Cl(2)–Ru–S(2)	86.34(7)	S(2)–Ru–S(3)	92.48(7)	C(1)–P–C(7)	111.5(3)
Cl(2)–Ru–S(3)	93.10(7)	Cl(3)–Ru–Cl(4)	89.86(7)	C(1)–P–C(15)	113.4(3)	C(1)–P–C(23)	102.3(3)
Cl(3)–Ru–S(1)	91.24(7)	Cl(3)–Ru–S(2)	172.72(7)	C(7)–P–C(15)	110.1(3)	C(7)–P–C(23)	115.1(3)
Cl(3)–Ru–S(3)	87.31(7)	Cl(4)–Ru–S(1)	85.67(7)	C(15)–P–C(23)	104.1(3)		
Cl(4)–Ru–S(2)	90.54(7)	Cl(4)–Ru–S(3)	176.70(8)				
Compound **4b**							
Ru–P(1)	2.257(2)	Ru–S(1)	2.250(2)	Ru–S(2)	2.216(2)		
Ru–Cl(1)	2.482(2)	Ru–O(2)	2.089(4)	Ru–O(4)	2.084(4)		
S(1)–O(5)	1.470(7)	S(2)–O(6)	1.398(6)	O(1)–C(2)	1.364(7)		
O(2)–C(6)	1.315(7)	O(3)–C(9)	1.379(8)	O(4)–C(13)	1.308(7)		
P(2)–C(25)	1.816(6)	P(2)–C(33)	1.790(6)	P(2)–C(41)	1.791(7)		
P(2)–C(47)	1.818(6)						
Cl(1)–Ru–S(1)	88.06(7)	Cl(1)–Ru–S(2)	91.55(6)	O(2)–C(6)–C(1)	122.2(5)	P(1)–C(1)–C(6)	109.9(4)
Cl(1)–Rh–S(1)	165.96(6)	Cl(1)–Ru–O(2)	87.8(1)	Ru–P(1)–C(1)	102.3(2)	Ru–O(4)–C(13)	118.5(3)
Cl(1)–Ru–O(4)	88.0(1)	S(1)–Ru–S(2)	94.75(6)	O(4)–C(13)–C(8)	123.4(5)	P(1)–C(8)–C(13)	112.6(5)
(1)–Ru–P(1)	99.06(7)	S(1)–Ru–O(2)	88.8(1)	Ru–P(1)–C(8)	101.2(2)	C(25)–P(2)–C(41)	114.5(3)
S(1)–Ru–O(4)	175.2(1)	S(2)–Ru–P(1)	99.84(6)	C(25)–P(2)–C(33)	108.7(3)	C(25)–P(2)–C(41)	114.5(3)
S(2)–Ru–O(2)	176.4(1)	S(2)–Ru–O(4)	88.2(1)	C(33)–P(2)–C(41)	110.4(3)	C(33)–P(2)–C(47)	113.5(3)
P(1)–Ru–O(2)	80.3(1)	P(1)–Ru–O(4)	84.2(1)	C(41)–P(2)–C(47)	103.9(3)		
O(2)–Ru–O(4)	88.3(1)	Ru–O(2)–C(6)	119.7(4)				

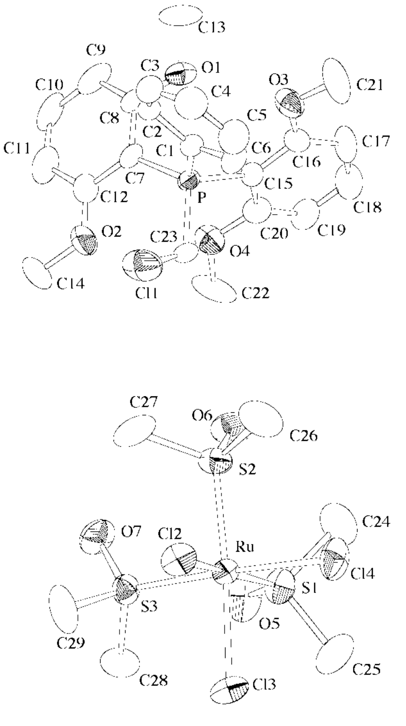


Fig. 1 An ORTEP[21] diagram of a cation and an anion of complex **3b** with thermal ellipsoids drawn at the 50% probability level (as in all figures).

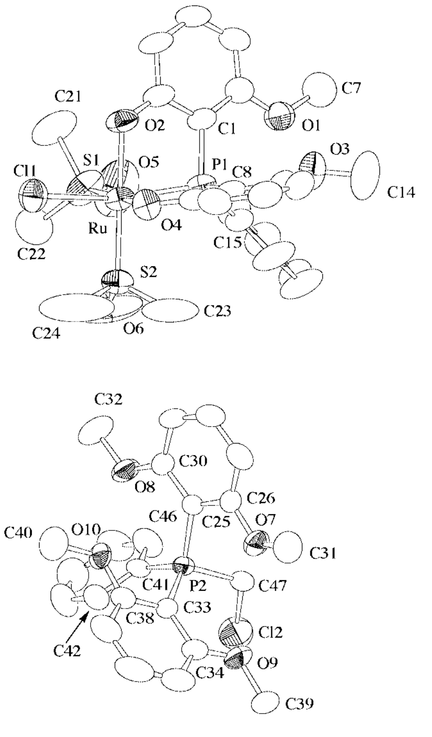


Fig. 2 An ORTEP diagram of a cation and an anion of complex **4b**.

Carbon monoxide was bubbled into a solution of complex **2** in CH$_2$Cl$_2$ for *ca.* 5 min at room temperature. A white precipitate formed rapidly, and a small amount of yellow crystals **6** was isolated from the reaction solution (Scheme 1). The white solid was insoluble in various solvents and its IR spectrum showed the presence of terminal carbonyl bands (2010 and 1983 cm^{-1}). The molecule is assumed to be polymeric but the structure is unknown at present. The FAB mass spectrum of **6** showed a molecular peak at *m*/*z* 844 corresponding to [RuCl$_2$(MDMPP)$_2$(CO)]. The IR spectrum showed a band at 1962 cm^{-1} assignable to a terminal carbonyl group. X-Ray crystallographic analysis showed that one of the MDMPP groups acts as a P,O-bidentate ligand and the other one as a monodentate ligand (Fig. 5). The two phosphorus atoms and two chlorine atoms are each mutually *trans* showing that a *cis*-to-*trans* isomerization had occurred in the equatorial plane. This can be

Table 3 Selected bond lengths (Å) and angles (°) of *mer*-[$RuCl_2$(MDMPP)(XylNC)$_3$] **5a** and *mer*-[$RuCl_2$(MDMPP)(MesNC)$_3$] **5b**

Compound **5a**		Compound **5b**	
Ru(1)–Cl(1)	2.434(2)	Ru(1)–Cl(1)	2.423(2)
Ru(1)–Cl(2)	2.421(2)	Ru(1)–Cl(2)	2.439(2)
Ru(1)–P(1)	2.401(2)	Ru(1)–P(1)	2.408(2)
Ru(1)–C(21)	1.985(9)	Ru(1)–C(21)	2.008(9)
Ru(1)–C(30)	1.966(9)	Ru(1)–C(31)	1.967(9)
Ru(1)–C(39)	2.002(8)	Ru(1)–C(41)	1.989(9)
C(21)–N(1)	1.162(10)	C(21)–N(1)	2.008(9)
C(30)–N(2)	1.17(1)	C(31)–N(2)	1.16(1)
C(39)–N(3)	1.146(9)	C(41)–N(3)	1.16(1)
Cl(1)–Ru(1)–Cl(2)	174.18(9)	Cl(1)–Ru(1)–Cl(2)	174.56(8)
Cl(1)–Ru(1)–P(1)	93.52(8)	Cl(1)–Ru(1)–P(1)	92.59(8)
Cl(1)–Ru(1)–C(21)	92.0(2)	Cl(1)–Ru(1)–C(21)	88.1(2)
Cl(1)–Ru(1)–C(30)	88.2(3)	Cl(1)–Ru(1)–C(31)	87.4(3)
Cl(1)–Ru(1)–C(39)	93.1(2)	Cl(1)–Ru(1)–C(41)	86.9(3)
Cl(2)–Ru(1)–P(1)	92.29(8)	Cl(2)–Ru(1)–P(1)	92.84(8)
Cl(2)–Ru(1)–C(21)	87.5(2)	Cl(2)–Ru(1)–C(21)	92.0(2)
Cl(2)–Ru(1)–C(30)	86.0(3)	Cl(2)–Ru(1)–C(31)	87.2(3)
Cl(2)–Ru(1)–C(39)	87.0(2)	Cl(2)–Ru(1)–C(41)	92.4(3)
P(1)–Ru(1)–C(21)	91.8(2)	P(1)–Ru(1)–C(21)	91.4(2)
P(1)–Ru(1)–C(30)	177.7(2)	P(1)–Ru(1)–C(31)	176.7(3)
P(1)–Ru(1)–C(39)	92.6(2)	P(1)–Ru(1)–C(41)	94.9(2)
C(21)–Ru(1)–C(30)	89.7(3)	C(21)–Ru(1)–C(31)	85.3(3)
C(21)–Ru(1)–C(39)	173.0(3)	C(21)–Ru(1)–C(41)	172.1(3)
C(30)–Ru(1)–C(39)	85.7(3)	C(31)–Ru(1)–C(41)	88.3(3)
Ru(1)–C(21)–N(1)	174.5(7)	Ru(1)–C(21)–N(1)	172.8(7)
C(21)–N(1)–C(22)	170.0(8)	C(21)–N(1)–C(22)	169.4(9)
Ru(1)–C(30)–N(2)	176.8(7)	Ru(1)–C(31)–N(2)	177.4(8)
C(30)–N(2)–C(31)	171.8(8)	C(31)–N(1)–C(32)	175.8(9)
Ru(1)–C(39)–N(3)	172.0(7)	Ru(1)–C(41)–N(3)	171.9(7)
C(39)–N(3)–C(40)	170.1(8)	C(41)–N(1)–C(42)	169.1(9)

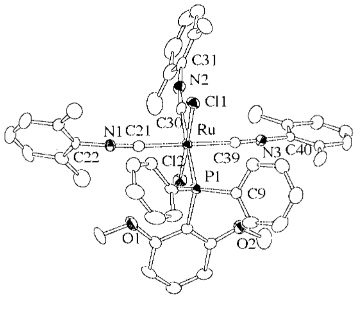


Fig. 3 An ORTEP diagram of complex **5a**.

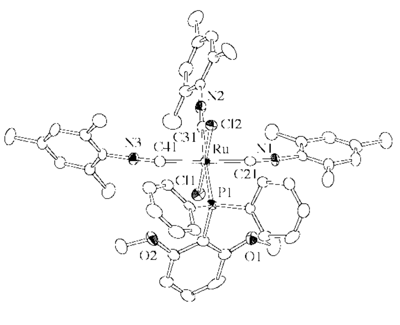


Fig. 4 An ORTEP diagram of complex **5b**.

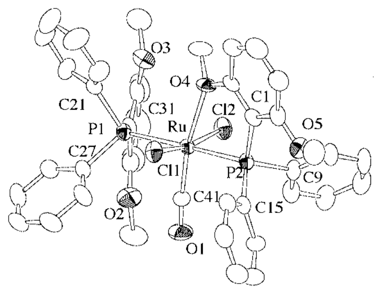


Fig. 5 An ORTEP diagram of complex **6**.

explained by the stereospecific addition of CO to a five-coordinate intermediate formed by initial dissociation of one of the ether oxygen atoms. The ^1H NMR spectrum showed only one singlet at δ 3.53 for methoxy groups, incompatible with the structure in the solid state, due to rapid ligand exchange among four methoxy groups.

Crystal structures

Complexes 3b and 4b. Perspective drawings of complexes **3b** and **4b** are illustrated in Figs. 1 and 2. Selected bond lengths and angles are listed in Table 2. The molecules of **3b** and **4b** consist of the discrete salts; the anions are [$RuCl_3$(DMSO-*S*)$_3$]$^-$ for **3b** and [RuCl(DMSO-*S*)$_2${PPh(C_6H_3OMe-6-O-2)$_2$-*P*,*O*,*O′*)]$^-$ for **4b** , and the cation has a common structural unit [BDPMPP(CH_2Cl)]$^+$.

The geometry of the anion of complex **3b** has a facial octahedral structure and the A–Ru–B angles between *cis* ligands fall in the range 86–93°. The average Ru–Cl and Ru–S bond lengths are 2.430 and 2.269 Å, respectively. These bond lengths were in agreement with those in the anionic part of [NH_2Me_2][$RuCl_3$(DMSO)$_3$].[22]

The Ru atom in the anion of complex **4b** is in a distorted octahedral configuration and is surrounded by two DMSO molecules, a Cl anion and a tridentate P,O,O′ ligand derived from demethylation of two methoxy groups of BDMPP. The Cl atom is *trans* to the P atom (Fig. 2). The S–Ru–P and S–Ru–S angles are *ca.* 99 and 95°, respectively. These larger than ideal angles are traced back to the P–Ru–O angles of *ca.* 84°, which arise from liberation of steric interaction between DMSO ligands and the phosphorus ligand, and the formation of the five-membered chelate rings. Other angles around the Ru atom are near 90°. The Ru–O bond distances of 2.09 Å are similar to those of other ruthenium complexes.[7] The Ru–S(1) length of 2.250(2) Å and Ru–S(2) of 2.216(2) Å are slightly shorter than those in **3b**, suggesting that the *trans* influence of a Cl ligand is higher than that of a O ligand. The S(2)–O(6) distance of 1.398(6) Å is shorter by 0.07 Å in comparison with those in **3b**. The Ru–Cl bond length in **4b** is longer by 0.21 Å than the average bond length of **3b**, suggesting that phosphine has a greater *trans* influence than the DMSO ligand. A similar trend has been observed in DMSO complexes of platinum.[23] The O(2)–C(6) and O(4)–C(13) bond lengths are shorter by 0.07 Å than those of the O(1)–C(2) and O(3)–C(9) lengths.

The cations in complexes **3b** or **4b** are typical of those in phosphonium salts. The geometry around the P(2) atom is quasi-tetrahedral.

Complexes 5a and 6b. Selected bond lengths and angles are listed in Table 3. The adjacent A–Ru–B bond angles of **5a** and **5b** fall in the range 90 ± 3°, and the molecules adopt an octahedral configuration. Three isocyanide ligands occupy the meridional positions and two Cl atoms are in mutually *trans* positions. The Ru–C bond length (1.966 Å) of isocyanide at the *trans* position to the phosphine ligand is not significantly different from other Ru–C bond lengths of *ca.* 2.000 Å. The Ru–C–N and C–N–C bond angles in isocyanide ligands are near the ideal values.

Complex 6. Selected bond lengths and angles are listed in Table 4. Two P and two Cl atoms each occupy mutually *trans* positions. The CO ligand is in a *trans* position to the ether oxygen atom (Fig. 5). The Ru–O(4) bond length of 2.270 Å is longer by 0.03 Å than those found in **2**.[7b] The Ru–P(2) bond length (2.339 Å) in the chelated ligand is shorter than non-chelated Ru–P(1) of 2.422 Å, resulting in different

Table 4 Selected bond lengths (Å) and angles (°) of [RuCl$_2$(MDMPP)(MDMPP-κ^2*P*,*O*)(CO)] **6**

Ru–Cl(1)	2.393(2)	Ru–Cl(2)	2.381(2)
Ru–P(1)	2.422(2)	Ru–P(2)	2.339(2)
Ru–O(4)	2.270(5)	Ru–C(41)	1.810(7)
C(41)–O(1)	1.142(9)	O(2)–C(34)	1.363(9)
O(3)–C(38)	1.38(1)	O(4)–C(2)	1.403(9)
O(5)–C(6)	1.339(9)		
Cl(1)–Ru–Cl(2)	168.84(7)	Cl(1)–Ru–P(1)	91.18(7)
Cl(1)–Ru–P(2)	85.28(7)	Cl(1)–Ru–O(4)	84.5(2)
Cl(1)–Ru–C(41)	97.3(3)	Cl(2)–Ru–P(1)	89.97(7)
Cl(2)–Ru–P(2)	93.59(7)	Cl(2)–Ru–O(4)	87.4(3)
Cl(2)–Ru–C(41)	93.8(3)	P(1)–Ru–P(2)	176.44(8)
P(1)–Ru–O(4)	101.8(1)	P(1)–Ru–C(41)	89.0(2)
P(2)–Ru–O(4)	78.3(1)	P(2)–Ru–C(41)	91.0(2)
Ru–O(4)–C(2)	117.3(4)	O(4)–C(2)–C(1)	118.0(2)
Ru–P(2)–C(1)	102.4(2)	P(2)–C(1)–C(2)	117.8(6)
Ru–C(41)–O(1)	175.9(2)		

co-ordination modes, and is longer by 0.1 Å than the corresponding bond lengths in **2**,[7b] due to the greater *trans* influence of the phosphorus ligand than the ether O.

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