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Chemistry of $[Cp^*RuOMe]_2$

XI *. Reactions with $P(OMe)_3$

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Abstract

Addition of $P(OMe)_3$ to $[Cp^*RuOMe]_2$ (**1**) gave the new Cp^*Ru complexes $(Cp^*RuOMe)_2(P(OMe)_3)$ (**2**), $Cp^*Ru\ (P(OMe)_3)_2OMe$ (**3**) and $Cp^*Ru(P(OMe)_3)_2(PO(OMe)_2)$ (**5**). **3** was converted slowly into the hydride $Cp^*Ru(P(OMe)_3)_2H$ (**4**). Reaction of either **3**, **4** or the cationic trisphosphite complex $[Cp^*Ru(P(OMe)_3)_3]CF_3SO_3$ (**7**), with NaI gave the iodo complex $Cp^*Ru(P(OMe)_3)_2I$ (**6**).

Introduction

The ready addition of ligands to the coordinatively unsaturated dimer $[Cp^*RuOMe]_2$, **1**, has been amply demonstrated [1–4]. Whereas diphosphines react without cleavage of the dimer to yield the dimeric adducts $(Cp^*RuOMe)_2$dppm [3], simple phosphines, CO, or nitrogen bases such as bipyridine cleave the dimer to give the monomeric complex type $Cp^*RuL_2(OMe)$ or derivatives thereof [3,4]. In contrast, the addition of $P(OMe)_3$ was found to proceed stepwise, and the addition products undergo further transformations under mild conditions as described below.

Results

A pentane or ether solution of **1** in the presence of up to 6 molar proportions of $P(OMe)_3$ yields a binuclear monoadduct of composition $(Cp^*RuOMe)_2(P(OMe)_3)$, **2**. Monitoring of the reaction by ^1H NMR spectroscopy reveals the presence of a mixture of **1** and **2** after addition of the first portions of $P(OMe)_3$ and finally a mixture of **2** and **3** (see below) along with free $P(OMe)_3$. Complex **2** is characterized by an OMe signal shifted upfield by 0.2 ppm with respect to **1**, a $P(OMe)_3$

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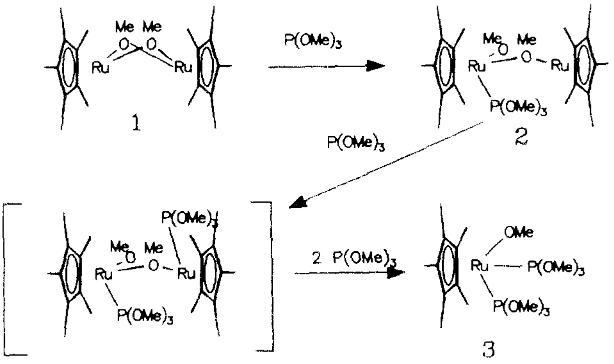
* For Part X, see ref. 1.



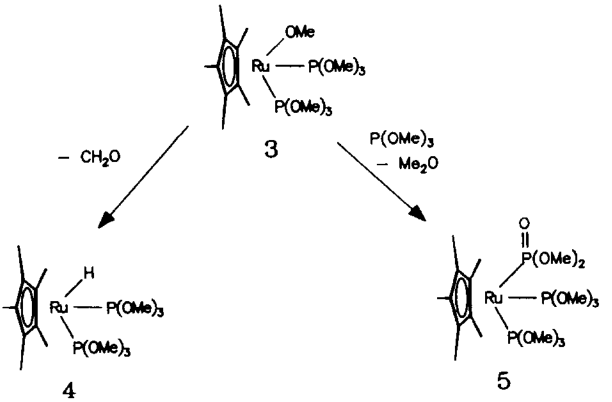
Scheme 1.

doublet, and two Cp* signals, a singlet (δ 1.65 ppm) and a doublet (δ 1.61 ppm, $J(CH_3P)$ 2.1 Hz) in the correct integration ratio, clearly indicating that it is the monoadduct. The appearance of separate sharp signals for the two different Cp* ligands in the presence of an excess of $P(OMe)_3$, separated by only 0.04 ppm, indicate that the product is kinetically inert at ambient temperature on the NMR timescale ($k_1 < 1$ s^{-1}), where neither intermolecular exchange nor an intramolecular shift of the $P(OMe)_3$ group to the neighbouring, coordinatively-unsaturated Ru atom occurs. Complex **2** is of limited thermal stability. It can be crystallized from pentane (see Experimental section) but tends to decompose on standing. All crystals examined on the X-ray diffractometer turned out to be twinned. It is noteworthy that PMe_3 under similar conditions gave only $Cp^*Ru(PMe_3)_2OMe$, with no indications of a monoadduct.

No bisphosphite adduct to **1** could be detected in the NMR spectrum. In all cases where addition to **1** occurs without cleavage of the methoxo bridge, *cis*-$[Cp^*RuL(OMe)]_2$ complexes had been obtained [1,4]. The formation of a bis-*cis* adduct of $P(OMe)_3$ may be unfavourable on steric grounds. On the other hand, $P(OMe)_3$ appears not strong enough as a ligand to directly cleave the dimer, thus allowing observation of the first example of a monoadduct of **1**.

Use of a larger excess of $P(OMe)_3$, at 0°C, gave the monomeric cleavage product $Cp^*Ru(P(OMe)_3)_2OMe$, **3**. At least 8 equivalents of $P(OMe)_3$ are necessary to achieve complete conversion of **1** into **3**. The OMe signal in **3** is again shifted upfield and now appears at 3.69 ppm (Table 1), indicating a terminal methoxo ligand. The $P(OMe)_3$ protons resonate as a pseudo-triplet (${}^3J$(H–P) = 11 Hz) due to strong P–P coupling giving an isospin = 1 system. Complex **3** is air sensitive and also of limited thermal stability at ambient temperature. On standing, it is slowly converted, even as a solid, into the hydride **4** (Scheme 2). This very common transformation of alkoxides of the Pt-metals into hydrides by β-elimination of aldehyde [5,6] does not occur readily with **1**, but does so with its addition products Cp^*RuL_2OMe. Hydride **4** shows a characteristic triplet at high field (−12.8 ppm, Table 1) for the hydridic proton along with the expected Cp* and $P(OMe)_3$ signals.

Finally, a still larger excess of $P(OMe)_3$ (9 mole per Ru) reacted with **1** at ambient temperature to give the bisphosphite(phosphonate) complex $Cp^*Ru(P(OMe)_3)_2(PO(OMe)_2)$, **5**, in good yield. The formation of **5** can be understood as

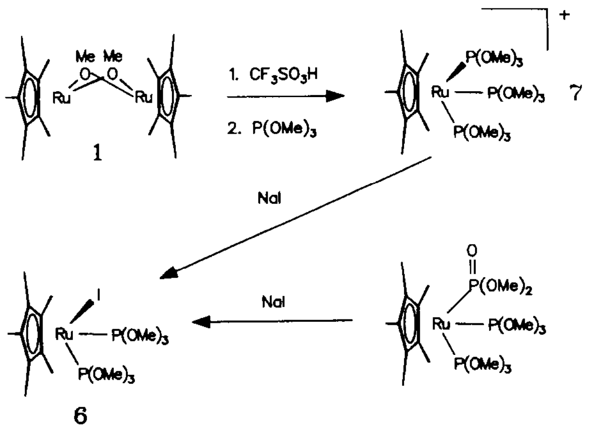


Scheme 2.

involving an inter- or intra-molecular Arbuzhov rearrangement [7] of one phosphite ligand, with the highly polarized OMe group acting as the nucleophile, leading to the elimination of Me_2O. The Cp* ligand in **5** appears as a somewhat unsymmetrical quartet, indicating similar coupling to phosphite and phosphonate phosphorus atoms. The POMe signals show up as a pseudotriplet and a doublet with the signals in a 3 : 1 integration ratio. Complex **5** is slightly air sensitive in solution and as a solid, but appears to be thermally stable.

Whereas this first intramolecular Arbuzhov rearrangement proceeded under rather mild conditions, attempts to bring about further rearrangement of **5** in the same sense by using NaI in acetone, which had furnished bis- and tris-phosphonate complexes of a variety of transition metal moieties [8], was unsuccessful in the present case. Nucleophilic displacement of the phosphonate group gave the corresponding iodo complex $Cp^*Ru(P(OMe)_3)_2I$, **6**, instead.

Similarly the cationic trisphosphite complex $[Cp^*Ru(P(OMe)_3)_3]^+$, **7**, which was prepared according to Scheme 3 from **3** generated *in situ* by treatment with CF_3SO_3H in the presence of an excess of $P(OMe)_3$, and was isolated and



Scheme 3.

Table 1

^1H and ^{31}P NMR parameters ($\delta(^1H)$/ppm (J/Hz), $\delta(^{31}P$/ppm)) for complexes **2**–**7**

Complex	No.	Cp*	P(OMe)$_3$	others
(Cp*RuOMe)$_2$(P(OMe)$_3$)	**2**	1.62	3.69 (11.2) 151.6	4.07 (OMe)
Cp*Ru(P(OMe)$_3$)$_2$(OMe)	**3**	1.73 (2.1)	3.58 (11.0) 155.0	3.69 (OMe)
Cp*Ru(P(OMe)$_3$)$_2$H	**4**	2.04 (2.1, 0.5 [a])	3.44 (11.6) 170.7	−12.8 (H)
Cp*Ru(P(OMe)$_3$)$_2$(PO(OMe)$_2$)	**5**	1.85 (2.1)	3.55 (11.1) 156.6 (d), 107.0 (t), 10.3)	3.68 (PO(OMe)$_2$)
Cp*Ru(P(OMe)$_3$)$_2$I	**6**	1.76 (2.4)	3.52 (11.6) 156.6	
[Cp*Ru(P(OMe)$_3$)$_2$]CF$_3$SO$_3$	**7**	1.73 (2.5)	3.67 (11.2) 150.6	

[a] ^3J(HCRuP), ^3J(HCRuH).

characterized as the CF_3SO_3-salt, gave **6** on treatment with iodide instead of undergoing an Arbuzov reaction.

Experimental

All operations were performed under pure, dry nitrogen by standard Schlenk technique. NMR was run on Bruker SY 80 FT, mass spectra on a Varian CH5 DF, and IR spectra on Perkin–Elmer 842 FT Instruments.

*Bis[μ-methoxo(pentamethylcyclopentadienyl)ruthenium]trimethylphosphite, (Cp*RuOMe)$_2$(P(OMe)$_3$) (2).* To a solution of 0.35 g (0.565 mmol) of bis[μ-methoxo(pentamethylcyclopentadienyl)ruthenium], **1**, in 50 ml of pentane was added 0.5 g (3.95 mmol) of P(OMe)$_3$. The colour of the solution immediately changed from cherry red to red brown. After a few minutes at ambient temperature the solution was filtered and cooled to −80°C. Complex **2** separated overnight as dark red crystals, which were isolated and dried *in vacuo*. Yield was 82%. The mass spectrum of **2** was identical with that of **1** (so showing no molecular ion).

*Pentamethylcyclopentadienyl(bis(trimethylphosphite)(methoxo)ruthenium, Cp*Ru-(P(OMe)$_3$)$_2$OMe (3).* To a solution of 0.135 g (0.25 mmol) of **1** in 30 ml pentane, cooled to 0°C, was added 0.25 g (2.02 mmol) of P(OMe)$_3$. During 5 h the colour changed to light brown. After filtration the solvent was stripped and the excess of P(OMe)$_3$ was evaporated off *in vacuo*. The residue was recrystallized from pentane. Cooling of a concentrated pentane solution gave 60% of **3** as a yellow solid. MS (m/e, I_{rel}%): 516 (4, M^+), 486 (100, $M - CH_2O$), 470 (14, $M - Me_2O = M'$), 455 (27, $M' -$ OMe), 360 (30, $M -$ P(OMe)$_3$ − OMe), 345 (90, Cp*RuPO(OMe)$_2$). Anal. Found: C, 39.08; H, 6.75. $C_{17}H_{36}O_7P_2Ru$ calcd. (M_r 515.5): C, 39.60, H, 7.05%.

*Pentamethylcyclopentadienyl(bis(trimethylphosphite))hydridoruthenium, Cp*Ru-(P(OMe)$_3$)$_2$H (4).* To a solution of 0.123 g (0.23 mmol) of **1** in 30 ml MeOH was added 1.2 g (9.65 mmol) of P(OMe)$_3$. The solvent was removed on a water bath at 40°C by applying a gentle vacuum. The residual oily solid, which partly crystallized on standing, was redissolved in pentane. Cooling of the solution to −80°C gave about a 20% yield of the product as light brown crystals. IR (KBr): 1925m cm^{-1} (Ru–H). MS (m/e, $I_{rel}\%$): 486 (100, M^+), 455 (16, $M-$OMe), 345 (40, $Cp^*RuPO(OMe)_2$). Anal. Found: C, 37.7; H, 7.35. $C_{16}H_{34}O_6P_2Ru$ calcd. (M_r 485.5): C, 39.6, H, 7.06%.

*Pentamethylcyclopentadienyl(bis(trimethylphosphite))(dimethylphospinito-*P*-)ruthenium,* $Cp^*Ru(P(OMe)_3)_2(PO(OMe)_2)$ *(5).* To a solution of 0.358 g (0.67 mmol) of **1** in 35 ml of pentane was added 1.485 g (12 mmol) of $P(OMe)_3$. After 3 h the brown mixture was filtered and the solvent evaporated *in vacuo*. The excess of $P(OMe)_3$ was removed under high vacuum. The product crystallized in 80% yield when a concentrated pentane solution was cooled to −80°C. MS (m/e, $I_{rel}\%$): 594 (96, M^+), 485 (85, $M-PO(OMe)_2$), 470 (100, $M-P(OMe)_3$), 360 (96, $Cp^*RuP(OMe)_3$), 345 (85, $Cp^*RuPO(OMe)_2$). Anal. Found: C, 36.60; H, 6.37. $C_{18}H_{39}O_9P_3Ru$ calcd.: (M_r 593.6): C, 36.42; H, 6.64%.

Pentamethylcyclopentadienyl(bis(trimethylphosphite))(iodo)ruthenium, $Cp^*Ru(P(OMe)_3)_2I$ *(6).* To 0.19 g (0.354 mmol) of **1** in 25 ml of ether was added 0.79 g (6.37 mmol) of $P(OMe)_3$ and then, after 5 min, 1.026 g (0.708 mmol) of NaI in 30 ml ether. After 17 h the reaction solution, now light brown, was filtered and the solvent evaporated. The residue was extracted with pentane. Cooling of the extract to −80°C gave 0.3 g (70%) of **6** as an orange yellow solid. Anal. Found: C, 31.77, H, 5.42. $C_{16}H_{33}IO_6P_2Ru$ calcd. (M_r 611.4): C, 31.43; H, 5.45%.

Pentamethylcyclopentadienyl(tris(trimethylphosphite))ruthenium-trifluoromethylsulfonate, $[Cp^*Ru(P(OMe)_3)_3]CF_3SO_3$ *(7).* A solution of **3** was prepared by adding 0.688 g (5.54 mmol) of $P(OMe)_3$ to 0.372 g (0.7 mmol) of **1** in 30 ml of ether and stirring the mixture for 3 h at 0°C. To this was added, with vigorous stirring, 0.25 g (1.67 mmol) of CF_3SO_3H in ether, whereupon the product separated as a brown precipitate. After 12 h at ambient temperature the precipitate was filtered off, washed with ether and twice with a few ml of water, and dried *in vacuo*. The cream-coloured powder was obtained in 60% yield. Anal. Found: C, 31.65; H, 5.7. $C_{20}H_{42}F_3O_{12}P_3SRu$ calcd. (M_r 757.7): C, 31.70, H, 5.6%.

Acknowledgments

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