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Preliminary communication

DISSOCIATION AND ISOMERIZATION OF $(OC)_5OsRu(CO)_3(SiCl_3)(Br)$, A COMPOUND WITH AN OSMIUM–RUTHENIUM DONOR–ACCEPTOR BOND

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Summary

In solution the donor–acceptor complex $(OC)_5OsRu(CO)_3(SiCl_3)(Br)$ (Ia) partially dissociates to $Os(CO)_5$ and $[Ru(CO)_3(SiCl_3)(Br)]_2$. On further standing in solution Ia isomerizes to $(Br)(OC)_4OsRu(CO)_4(SiCl_3)$.

We recently reported the preparation of $(OC)_5OsOs(CO)_3(GeCl_3)(Cl)$ (II) a compound in which the 18-electron complex $Os(CO)_5$ acts as a ligand toward the second osmium atom via a donor–acceptor metal–metal bond [1]. That the donor–acceptor metal–metal bond was unbridged by any ligands made II unique at the time amongst organometallic complexes. The compound was found to be surprisingly stable and was recovered unchanged after it had been heated in hexane at 125°C for 16 h. We have now prepared a number of analogues of this compound in which osmium or ruthenium acts as the acceptor atom. Some of the ruthenium complexes exhibit previously unobserved properties which are of general interest in both synthetic and mechanistic organometallic chemistry: some dissociate in solution, and some undergo facile isomerization to a form with a covalent, rather than dative, metal–metal bond. The compound $(OC)_5OsRu(CO)_3(SiCl_3)(Br)$ exhibits both these properties and is discussed here in detail.

Addition of a hexane solution of $Os(CO)_5$ [2] to one of *trans*-$Ru(CO)_4(SiCl_3)(Br)$ [3] at 0°C resulted in the quantitative formation of yellow, microcrystalline $(OC)_5OsRu(CO)_3(SiCl_3)(Br)$* (Ia) after 3 h. The structure of Ia was assigned the stereochemistry shown (eclipsed form drawn in this and other structures for convenience):

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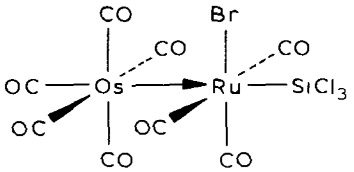
*Satisfactory microanalytical and mass spectral data have been obtained for all new compounds reported here.



(Ia)

This was done by analogy to the structure established for $(OC)_5OsOs(CO)_3(GeCl_3)(Cl)$ [1] and the known stereochemical course of the reactions of $Ru(CO)_4(SiRCl_2)(X)$ (R = Me, Cl; X = H, halogen, $SiRCl_2$) [3,4]. The ^{13}C NMR spectrum of Ia in CH_2Cl_2/CD_2Cl_2 at −20°C was consistent with the proposed structure (approximate relative intensities are given in parentheses): δ 194.4 (2), 192.4 (1), 174.8 (4), 159.9 (1) ppm. (^{13}C NMR resonances of carbonyl groups bonded to second row transition metals are invariably to lower field than those due to carbonyls attached to the corresponding third row transition elements [5].)

The infrared spectrum (carbonyl region) of Ia in CH_2Cl_2 was similar to that of II with the exception that extra absorptions were observed at 2091.5, 2040.5, and 1985.5 cm^{-1} (Fig. 1). These absorptions lost intensity relative to the other bands when the spectrum was recorded at −20°C. The band at

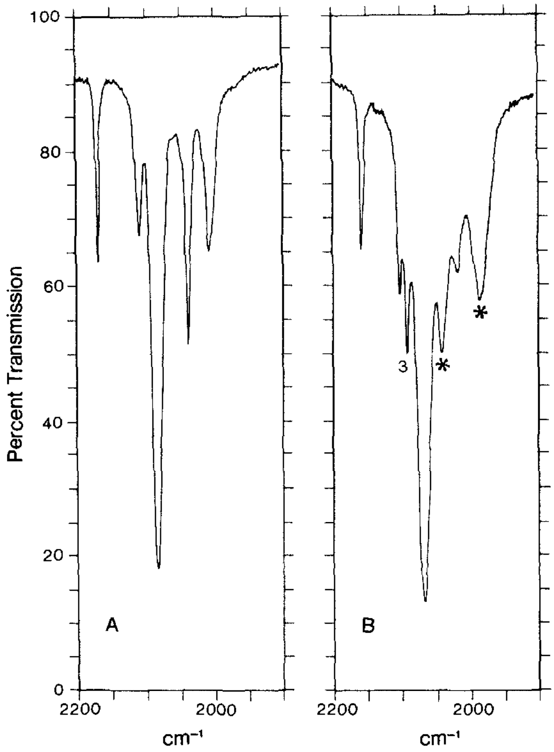


Fig. 1. Infrared spectrum (carbonyl region, CH_2Cl_2 solution) of (A) $(OC)_5OsOs(CO)_3(GeCl_3)(Cl)$; (B) $(OC)_5OsRu(CO)_3(SiCl_3)(Br)$ (the absorption marked 3 was assigned to $[Ru(CO)_3(SiCl_3)(Br)]_2$ and those marked with an asterisk to $Os(CO)_5$).

2091.5 cm^{-1} was assigned to $[Ru(CO)_3(SiCl_3)(Br)]_2$ (III) [3] (the other two CO stretches of this compound were assumed obscured by bands due to Ia); the other two bands were assigned to $Os(CO)_5$ [2]. When a sample of Ia was extracted with warm hexane, in which it was insoluble, the complete infrared spectrum (in the CO stretching region) of III and of $Os(CO)_5$ were clearly observed in the hexane extract. A ^{13}C NMR spectrum of Ia in CD_2Cl_2 at room temperature (Fig. 2) gave a signal at 183.0 ppm attributable to $Os(CO)_5$ [2]. Weak signals were observed at 186.7 and 186.9 ppm; these values were identical to those found for the ^{13}C NMR spectrum of III in the same solvent. The intensity of the signals could not be enhanced by longer accumulation times because of the isomerization of Ia (vide infra). These results are consistent with the following Lewis acid-Lewis base equilibrium for Ia in CH_2Cl_2 at room temperature.

$$2(OC)_5OsRu(CO)_3(SiCl_3)(Br) \rightleftharpoons 2Os(CO)_5 + [Ru(CO)_3(SiCl_3)(Br)]_2$$

It was also established that the equilibrium could be approached from the opposite direction, i.e., addition of a solution of $Os(CO)_5$ in hexane to one of III caused immediate formation of Ia. Also, treatment of solutions of Ia with PPh_3 rapidly gave the known compound $Ru(CO)_3(PPh_3)(SiCl_3)(Br)$ [3] and $Os(CO)_5$.

It is of relevance to mention here that there is considerable precedence for the dissociation in solution of molecules with covalent metal—metal bonds. Examples are known where both metals are transition metals [6] or where one of the metals is a nontransition metal [7] or metalloid [8]. However, in these cases the dissociation results in charged species. Homolysis of metal—metal bonds by ultraviolet irradiation to produce radicals is also well documented, e.g., ref. 9.

When Ia was stirred in CH_2Cl_2 solution at room temperature for 2 h it was converted to a different form, the mass spectrum and chemical analysis of which indicated that it also had the formula $RuOs(CO)_8(SiCl_3)(Br)$. The compound was, however, soluble in hexane (ν(CO) hexane: 2146.5(w), 2101(m), 2093.5(w), 2062(s), 2039.5(w), 2012.5(m) cm^{-1}). This suggested the new compound no longer possessed the donor— acceptor bond: all compounds we have so far prepared with donor—acceptor metal—metal bonds are insoluble in hexane (this is probably a consequence of the polar nature of the bond). The structure Ib is proposed for the isomerized product; the ^{13}C NMR spectrum of Ib in CD_2Cl_2 was consistent with this structure (Table 1; see also Fig. 2). Furthermore, reaction of Ib in hexane solution with I_2 gave $Os(CO)_4(Br)(I)$ as one product (Table 1); with Br_2 Ib gave the known compounds *cis*-$Os(CO)_4Br_2$ [10] and *trans*-$Ru(CO)_4(SiCl_3)(Br)$ (identified by infrared spectroscopy).

Treatment of $Ru(CO)_4(SiCl_3)(Br)$ with $M(CO)_4(PMe_3)$* (M = Ru, Os) similarly gave $(Me_3P)(OC)_4MRu(CO)_3(SiCl_3)(Br)$ (Table 1; data for Ru complex shown). There was no spectroscopic evidence for the dissociation of these compounds in solution nor did they react immediately with PPh_3. This is

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*These complexes were prepared by methods previously employed for the preparation of the analogous $M(CO)_4(PPh_3)$ derivatives [11].

TABLE 1

SPECTROSCOPIC DATA FOR NEW COMPOUNDS

Compound	ν(CO) (cm^{-1})	^{13}C NMR [a] (ppm) (CH_2Cl_2/CD_2Cl_2 soln)
$(OC)_5OsOs(CO)_3(GeCl_3)(Cl)$ [b]	2167.5m, 2106.5m, 2082s, 2035.5m, 2003.5 [c]	179.8(2), 170.3(1) 170.0(4), 157.5(1) [d]
$(OC)_5OsRu(CO)_3(SiCl_3)(Br)$ (Ia)	2156.5m, 2102w, 2067.5s, 2017.5m, 1985.5m [c,e]	194.4(2), 192.4(1), 174.8(4), 159.9(1) [d]
$(Br)(OC)_4OsRu(CO)_4(SiCl_3)$ (Ib)	2146.5w, 2101m, 2093.5w, 2062s, 2039.5w, 2012.5m [f]	194.8(4), 178.3(2), 169.2(1), 161.0(1)
$(OC)_5OsRu(CO)_3(SiCl_3)_2$	2158m, 2121.5w, 2090m, 2071.5s, 2027m [c,e]	196.0(2), 194.2(1), 173.4(4), 158.6(1) [d]
$(Me_3P)(OC)_4RuRu(CO)_3(SiCl_3)(Br)$	2123w, 2079m, 2041.5s, 2005.5w [c]	200.2(4, 6.8), 198.2(2), 196.7(1)
$(Br)(Me_3P)(OC)_3RuRu(CO)_4(SiCl_3)$	2128w, 2079w, 2063m, 2047s, 2011m, 1988m [f]	201.8(2, 8.9), 199.4(4), 196.6(1, 5.2)
$(Me_3P)(OC)_4OsRu(CO)_3(SiCl_3)_2$	2127w, 2067.5w, 2039.5s, 2002m [c]	198.6(2), 196.7(1), 182.4(4, 4.1)
$(H)(Me_3P)(OC)_3RuRu(CO)_4(SiCl_3)$	2117w, 2062.5vw, 2041sh, 2039vs, 2008sh, 2005.5m 1983.5s [f]	203.8(2, 10.3), 202.1(4), 199.4(1, 5.5) [g]
$Os(CO)_4(Br)(I)$	2175m, 2108.5vs, 2094.5s 2057.5vs [c]	(not measured)

[a] Carbonyl region; first figure in parentheses is the approximate intensity, second figure (where applicable) is J(PC). [b] Ref. 1. [c] CH_2Cl_2 soln. [d] Recorded at −20°C. [e] Bands assigned to known dissociation products omitted. [f] Hexane soln. [g] Benzene-d_6 soln.

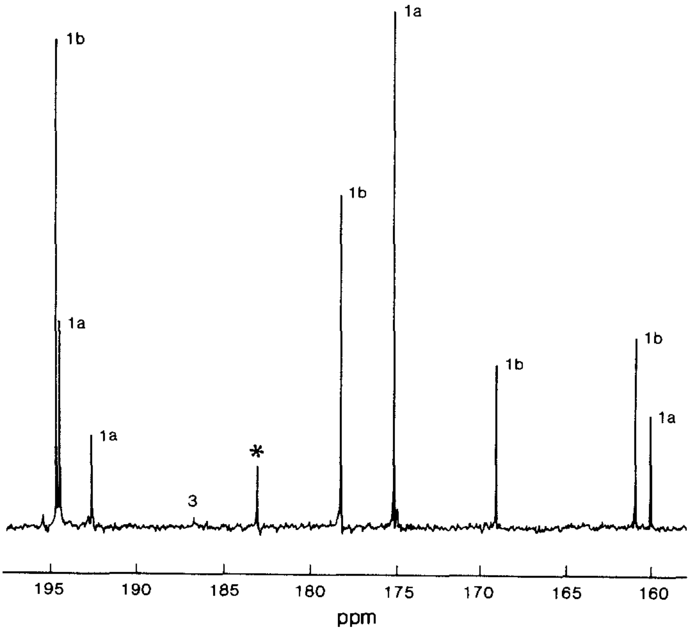
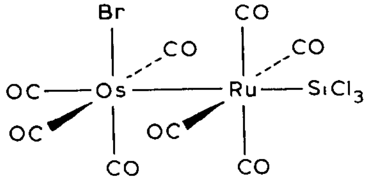


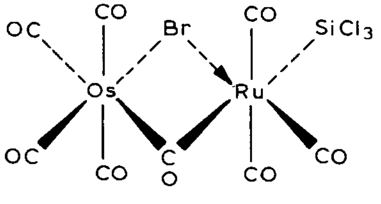
Fig. 2. 100.6 MHz ^{13}C NMR spectrum of I in CD_2Cl_2/CH_2Cl_2 (16 h accumulation time, during which Ia isomerized to Ib). The notation used for the assignment of the resonances is the same as that used in the text and Fig. 1.



(I b)

consistent with the anticipated increased donor properties of the $M(CO)_4$-(PMe_3) unit due to the presence of the basic trimethylphosphine ligand. The ^{13}C NMR spectra of these derivatives indicated that the PMe_3 ligand occupied the site *trans* to the metal—metal bond. These complexes did, however, isomerize with approximately the same rate as did Ia when stirred in solution.

The reaction of *cis*-$Ru(CO)_4(SiCl_3)_2$ [4] in hexane with $Os(CO)_5$ gave $(OC)_5OsRu(CO)_3(SiCl_3)_2$ (IV). The infrared spectrum of this compound in CH_2Cl_2 indicated that partial dissociation to give $Os(CO)_5$ had also occurred. (It has not been established how the other 16-electron half of the molecule is stabilized; the $SiCl_3$ group is not known to act as a bridging ligand). In contrast to the bromo compounds, IV and $(Me_3P)(OC)_4OsRu(CO)_3(SiCl_3)_2$ appeared not to isomerize in solution; slow decomposition over 48 h took place when they were stirred in solution.



(Ic)

The isomerization of Ia may be related to the ability of the bromo group to act as a bridging ligand and an intermediate shown in Ic may be involved in the process. A change in the formal oxidation state of each metal accompanies the isomerization and the proposed intermediate has similarities to the intermediates believed to be involved in inner-sphere electron transfer processes of classic coordination complexes [12]. It may, as suggested by a referee, also be regarded as an oxidative-addition of RuBr unit to the coordinatively unsaturated d^8 M(O) complex $Os(CO)_5$. After the exchange of ligands, the silyl ligand is in a position *cis* to the metal—metal bond and an isomerization is required to produce the observed product. Nondissociative *cis-trans* isomerization is, however, a feature of compounds of this type [3,13].

Reaction of $Ru(CO)_4(PMe_3)$ with *cis*-$Ru(CO)_4(SiCl_3)(H)$ [3] gave the hexane-soluble $Ru_2(CO)_7(PMe_3)(SiCl_3)(H)$ (V) directly (Table 1). The ^1H NMR spectrum of this derivative (in C_6D_6) showed a doublet centred at δ −8.81 ppm (J(PH) 20.3 Hz). The value of the coupling is typical of a *cis* coupling of a phosphorus atom to a hydrogen atom attached to the same ruthenium atom [3]. The ^{13}C-{^1H} NMR spectrum in benzene-d_6 (Table 1) was consistent with this view. (The phosphorus couplings are also consistent with an isomerized product with the phosphine ligand *trans* to the ruthenium—ruthenium bond.) It therefore appears that the isomerized product results directly in this reaction which is in agreement with the marked tendency of the hydride moiety to act as a bridging ligand [14]. The mechanism of isomerization must, however, be different to that proposed for Ia since the hydride ligand lacks a lone pair of electrons.

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References

1 F.W.B. Einstein, R.K. Pomeroy, P. Rushman, and A.C. Willis, J. Chem. Soc., Chem. Commun., (1983) 854.
2 P. Rushman, G.N. van Buuren, M. Shiralian, and R.K. Pomeroy, Organometallics, 2 (1983) 693.
3 R.K. Pomeroy and X. Hu, Can. J. Chem., 60 (1982) 1279.
4 R.K. Pomeroy, R.S. Gay, G.O. Evans, and W.A.G. Graham, J. Amer. Chem. Soc., 94 (1972) 272; R.K. Pomeroy and K.S. Wijesekera, Inorg. Chem., 19 (1980) 3729.
5 B.E. Mann and B.F. Taylor, ^{13}C NMR Data for Organometallic Compounds, Academic Press, New York, 1981, p. 14.
6 D.A. Roberts, W.C. Mercer, S.M. Zahurak, G.L. Geoffroy, C.W. DeBrosse, M.E. Cass, and C.G. Pierpont, J. Am. Chem. Soc., 104 (1982) 911; L. Arndt, T. Delord, and M.Y. Darensbourg, ibid., 106 (1984) 456.
7 J.M. Burlitch, J. Am. Chem. Soc., 91 (1969) 4562; J.M. Burlitch, in G. Wilkinson, F.G.A. Stone, and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon, Oxford, 1982. Vol. 6, p. 1006.
8 W. Jetz and W.A.G. Graham, Inorg. Chem., 10 (1971) 1647.
9 M.S. Wrighton and D.S. Ginley, J. Am. Chem. Soc., 97 (1975) 2065; A. Hudson, M.F. Lappert, and B.K. Nicholson, J. Chem. Soc. Dalton Trans., (1977) 551.
10 F. L'Eplattenier and F. Calderazzo, Inorg. Chem., 6 (1967) 2092.
11 L.R. Martin, F.W.B. Einstein, and R.K. Pomeroy, Inorg. Chem., 22 (1983) 1959.
12 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 4th ed., Wiley, New York, 1980, p. 1210.
13 L. Vancea, R.K. Pomeroy, W.A.G. Graham, J. Am. Chem. Soc., 98 (1976) 1407.
14 J.R. Norton, Acc. Chem. Res., 12 (1979) 139.