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Kinetic and thermodynamic studies of carbon monoxide insertion in alkylosmium(II) complexes and comparison with iron(II) and ruthenium(II) isoelectronic complexes‡

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The equilibrium constants of the reaction of *cis,trans*-[Os(CO)$_2$(PMe$_3$)$_2$(Me)I] **1c** with carbon monoxide to give *cis,trans*-[Os(CO)$_2$(PMe$_3$)$_2$(COMe)I] **2c** have been measured and compared with the values obtained for the isoelectronic complexes of iron and ruthenium. The kinetics of the above reaction as well as of the analogous insertion reaction with $C_6H_{11}NC$, which affords *trans*-[Os(CO)(PMe$_3$)$_2$(C_6H_{11}NC)(COMe)I] **3**, has been investigated. The results are interpretable by the methyl migration mechanism. The crystal structure of the new complex **3** has been determined. Furthermore, the isomer *trans,trans*-[Os(CO)$_2$(PMe$_3$)$_2$(Me)I] **1t** has been synthesized by the photochemical isomerization of **1c** in the solid state. The spectroscopic properties of the *cis,trans* (**c**) and *trans,trans* (**t**) isomers for the triad Fe, Ru and Os are compared.

Carbon monoxide insertion in the metal–alkyl bond is a fundamental step in homogeneous catalysis with transition metals.[1] The mechanism of this reaction has been extensively studied[2] and the effects of the structures of the complexes and of the nature of the ligands on the reaction rate are in general well known.[3] On the contrary, comparative studies for isoelectronic complexes with metals of different Periods of the Periodic Table are rare,[4] and when a comparison of this type has been made it was usually from a qualitative point of view.[5]

These considerations prompted us to undertake a comparative study of the insertion of CO in the *cis,trans*-[M(CO)$_2$(PMe$_3$)$_2$(Me)I] (M = Fe, Ru or Os) complexes. Some kinetic and thermodynamic results for Fe[6,7] and Ru[8] have been reported previously. The kinetic results suggest differences in the reaction mechanisms on changing the metal: for the iron complex the reaction proceeds *via* a preliminary ionization of the Fe–I bond[9] with subsequent methyl migration; for the ruthenium complex the insertion proceeds *via* methyl migration with formation of a five-co-ordinated intermediate which, subsequently, reacts with CO. The reaction of the ruthenium complex is faster than that of iron. The thermodynamic results indicate that the stability of the acetyl complexes of iron is higher than that of the ruthenium complexes and inversely proportional to the strength of the metal–alkyl bond,[10] as expected from the literature data.[3]

In the present paper we report thermodynamic and kinetic results for the carbon monoxide insertion into *cis,trans*-[Os(CO)$_2$(PMe$_3$)$_2$(Me)I] which complete the series for isoelectronic complexes of Fe, Ru and Os. Furthermore, for a better understanding of the first step of the insertion reaction, we present also kinetic results on the reaction of this complex with $C_6H_{11}NC$ which affords the new complex [Os(CO)(PMe$_3$)$_2$(C_6H_{11}NC)(COMe)I] the structure of which has been solved by X-ray diffraction studies. Moreover, the photochemical synthesis of the complex *trans,trans*-[Os(CO)$_2$(PMe$_3$)$_2$(Me)I] is reported together with a comparison of the spectroscopic data for the *cis,trans* (**c**) and *trans,trans* (**t**) isomers for the triad Fe, Ru and Os.

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‡ *Non-SI unit employed*: atm = 101 325 Pa.

Experimental

Materials

The solvents (toluene, CH_2Cl_2, diethyl ether, *etc*.) were dried by standard methods.[11] Tetrahydrofuran (thf) was purified as described in ref. 12 and freshly distilled before use. Ethylene glycol dimethyl ether was purified with sodium thiosulfate and dried with $LiAlH_4$. Methyl iodide was purified as described in ref. 13. Trimethylphosphine was prepared following the method described by Wolfsberger and Schmidbaur.[14] The complex [Os(CO)$_3$(PMe$_3$)$_2$] was prepared by a slight modification of the method described in ref. 15: [$Os_3(CO)_{12}$] was treated with a solution of PMe$_3$ in diethyl ether at 140 °C in a Carius tube for 3 d; the yield of [Os(CO)$_3$(PMe$_3$)$_2$] was 80%, [Os(CO)$_4$(PMe$_3$)] was absent and the yield of the cluster [{Os(CO)$_3$(PMe$_3$)}$_3$] was 20%. The complex *cis,trans*-[Os(CO)$_2$(PMe$_3$)$_2$(Me)I] **1c** was prepared from [Os(CO)$_3$(PMe$_3$)$_2$(Me)]$^+$I$^-$ {derived by oxidative addition of MeI to [Os(CO)$_3$(PMe$_3$)$_2$]} in ethylene glycol dimethyl ether at 60 °C according to ref. 15.

Physical measurements

The IR spectra were obtained with a 1725X FT-IR Perkin-Elmer spectrophotometer or with a 983 Perkin-Elmer dispersive spectrophotometer, ^{1}H and ^{31}P-{H} NMR spectra on a Bruker AC 200 spectrometer. The ^{1}H chemical shifts are relative to tetramethylsilane as internal reference, ^{31}P-{H} to 85% H_3PO_4 in D_2O with a positive sign indicating a shift to a lower field. The elemental analyses were carried out with a Carlo Erba 1106 elemental analyser.

Reactivity of complex 1c with nucleophiles

No reaction was observed between complex **1c** and phosphines PMe$_3$, PPh$_3$, PEt$_3$ and PBu$^n_3$ in toluene at 25–140 °C or with *tert*-butyl isocyanide under the same conditions. Complex **1c** reacted with CO to give *cis,trans*-[Os(CO)$_2$(PMe$_3$)$_2$(COMe)I] **2c**, but this reaction did not go to completion up to P_{CO} = 1 atm at room temperature. Complex **2c** was characterized spectroscopically: $\tilde{\nu}_{max}$/cm^{-1} (hexane) 2026s and 1962s (CO) and 1578 (COCH$_3$); ^{1}H NMR (CD_2Cl_2) δ 2.51 (3 H, s, COCH$_3$) and 1.81 (18 H, t,[16] $|^2J_{PH} + {}^4J_{PH}|$ 4 Hz, PMe$_3$).

Synthesis of complexes

***trans*-[Os(CO)(PMe$_3$)$_2$(C$_6$H$_{11}$NC)(COMe)I] 3.** Complex **1c** (0.5 g) and an equimolar quantity of $C_6H_{11}NC$ were allowed to react in hexane (50 cm^3) at 30 °C. The reaction was completed in 15 h. The solvent was evaporated and the solid residue dissolved in CH_2Cl_2. Hexane was added until incipient precipitation; the solution obtained was allowed to crystallize at −18 °C. White crystals of complex **3** were obtained (yield 90%) (Found: C, 29.5; H, 4.85; N, 2.20. $C_{16}H_{32}INO_2OsP_2$ requires C, 29.6; H, 4.95; N, 2.15%). IR (hexane): $\tilde{\nu}_{max}$/cm^{-1} 1962 (CO), 1580 ($COCH_3$) and 2133 (CNC_6H_{11}). NMR (CD_2Cl_2): ^{1}H, δ 3.97 (1 H, m, 1H), 2.43 (3 H, s, $COCH_3$), 1.95 (4 H, m, $2CH_2$), 1.76 (4 H, m, $3CH_2$), 1.69 (18 H, t,[16] $|^2J_{PH} + {}^4J_{PH}|$ 6.7 Hz, PMe_3) and 1.43 (2 H, m, $4CH_2$); ^{31}P-{^{1}H}, δ −46.5 (s).

***cis,trans*-[Os(CO)$_2$(PMe$_3$)$_2$(C$_6$H$_{11}$NC)Me]BPh$_4$ 4.** Complex **3** (0.1 g) and an equimolar quantity of $Ag(O_3SCF_3)$ were dissolved in CH_2Cl_2 (20 cm^3). A slow formation of AgI was observed, which was filtered off. The solution evaporated to dryness, the residue dissolved in MeOH and complex **4** precipitated with $NaBPh_4$ as white crystals. Complex **4** was also obtained very slowly by reaction of **3** with $NaBPh_4$ in MeOH (yield 80%) without the addition of AgI (Found: C, 57.15; H, 6.35; N, 1.8. $C_{40}H_{52}BNO_2OsP_2$ requires C, 57.05; H, 6.25; N, 1.65%). IR (CH_2Cl_2): $\tilde{\nu}_{max}$/cm^{-1} 1989 and 2042 (CO) and 2204 (CNC_6H_{11}). NMR (CD_2Cl_2): ^{1}H, δ 7.32 (8 H, m, *o*-H), 7.04 (8 H, t, $^3J_{HH}$ 7.1, *m*-H), 6.91 (4 H, t, $^3J_{HH}$ 7.1, *p*-H), 3.95 (1 H, m, 1H), 1.99 (2 H, m, $4CH_2$), 1.65 (4 H, m, $2CH_2$), 1.39 (4 H, m, $3CH_2$), 1.72 (18 H, t,[16] $|^2J_{PH} + {}^4J_{PH}|$ 8.1, PMe_3) and −0.24 (3 H, t, $^3J_{PH}$ 8.1 Hz, CH_3); ^{31}P-{^{1}H}, δ −46.5 (s).

Attempts to obtain back complex **3** by the reaction of **4** and NBu_4I in CH_2Cl_2 were unfruitful.

Photochemical isomerization of complex 1c

The photochemical isomerization of complex **1c** was carried out with a 100 W tungsten lamp. In solution (hexane) decomposition of **1c** was observed with formation of [Os(CO)$_3$(PMe$_3$)$_2$] and [Os(CO)$_2$(PMe$_3$)$_2$I$_2$], characterized by their IR spectra.[15] In the solid state photochemical isomerization performed under N_2 for 10 d, afforded *trans,trans*-[Os(CO)$_2$(PMe$_3$)$_2$ (Me)I] **1t** (yield 10–15%). Complex **1t** was not isolated, but characterized spectroscopically: IR (hexane) $\tilde{\nu}_{max}$/cm^{-1} 1945vs and 2020vw (CO); ^{1}H NMR (CD_2Cl_2) δ 0.25 (3 H, t, $^3J_{HP}$ 4.9, CH_3) and 1.34 (18 H, t,[16] $|^2J_{PH} + {}^4J_{PH}|$ 3.8 Hz, PMe_3); ^{31}P-{^{1}H} NMR (CD_2Cl_2) δ −51.0 (s).

Equilibrium constants

The equilibrium constants (K_e) of the reaction between complex **1c** and carbon monoxide were measured in toluene in the temperature range 10–30 °C and at P_{CO} = 0.3–1.0 atm. The CO–N_2 mixtures were prepared as described in ref. 6. The concentration of CO, in solution, at different temperatures was interpolated from the literature data.[17] It was at least ten times higher than that of **1c**. In a typical run a solution of complex **1c** [(7–15) × 10^{-3} mol dm^{-3}] was saturated with the gas mixture; then an aliquot (10 cm^3) was introduced into a thermostatted reactor (300 cm^3) filled with the gas mixture. When equilibrium was reached the IR spectrum was measured in the CO stretching region. The concentration of **1c** was obtained by Beer's law from the two CO stretching bands. The concentration of **2c** was determined as the difference between the initial and equilibrium concentrations of **1c**. Owing to the slowness of the reaction (up to 60 d), adequate sealing of the reactor was important in order to obtain reproducible data. The experimental values of K_e are the means from at least three series of measurements.

Kinetic measurements

The reversible reaction between complex **1c** and carbon monoxide was monitored in toluene by IR spectroscopy in the temperature and CO pressure ranges 10–30 °C and 0.3–1 atm, respectively. The concentration of CO was at least ten times higher than that of **1c**. Owing to the slowness of the reaction it was monitored only up to 30% of the total transformation.

The reaction of complex **1c** with cyclohexyl isocyanide was monitored in toluene in the temperature range 10–40 °C. The cyclohexyl isocyanide concentration was at least ten times higher than that of **1c**. The kinetics were followed up to three half-lives.

Crystallography

A white prismatic crystal of complex **3** was used to determine cell parameters and for subsequent data collection. It was mounted on a computer-controlled Philips PW 1100 single-crystal diffractometer equipped with graphite-monochromatized Mo-Kα radiation (λ 0.710 69 Å) and the ω–2θ scan technique was used. The cell dimensions were determined by a least-squares refinement based on the setting angles of 25 reflections with 2θ ranging between 6 and 50°. Three standard reflections, measured periodically, showed no apparent variation in intensity during data collection. The data were corrected for Lorentz-polarization factors. A semiempirical absorption correction was applied on the basis of the variation in intensity during the azimuthal scans of some reflections according to the method of North *et al.*[18] The structure was solved by direct methods using the SIR 92[19] program package and refined by the full-matrix least-squares method with SHELXL 93.[20] Anisotropic thermal parameters were refined for Os, I and P atoms. Hydrogen atoms were included in idealized positions. The atomic scattering factors were taken from ref. 21.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/443.

Results and Discussion

Crystal structure of complex 3

Selected bond lengths and angles are given in Table 2. An ORTEP[22] view of complex **3** is shown in Fig. 1. The elementary cell contains eight molecules: the two molecules in the asymmetric unit **A** and **B** differ in the steric arrangement of the

Table 1 Crystal data and details of measurements for complex **3**

Formula	$C_{16}H_{32}INO_2OsP_2$
M	650
T/K	296
System	Monoclinic
Space group	$P2_1/c$
a/Å	14.665(2)
b/Å	20.129(2)
c/Å	16.278(2)
β/°	99.97(18)
U/(Å^3)	4732.6
Z	8
F(000)	2480
μ(Mo-Kα)/cm^{-1}	68.4
θ Range/°	3–20.07
ω-Scan width/°	1.8
hkl Octants explored	−14 to 13, 0–19, 0–15
Measured reflections	4106
Unique observed reflections [$I_o > 2\sigma(I_o)$]	2810
No. refined parameters	291
Goodness of fit on F^2	1.076
Final $R(F)$, $R'(F^2)$ indices [$I > \sigma(I)$]*	0.0448, 0.1158

* $R(F) = \Sigma||F_c| - |F_o||/\Sigma|F_o|$, $R'(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{\frac{1}{2}}$ with $w = 1/[\sigma^2(F_o^2) + (0.0725P)^2 + 78.21P]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

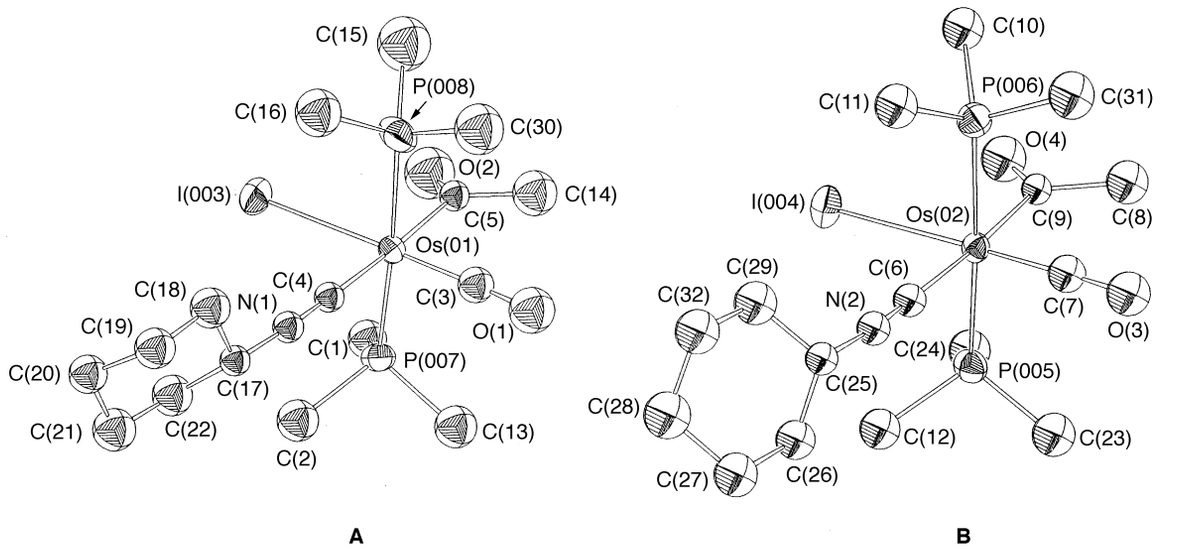


Fig. 1 An ORTEP drawing of complex **3**

Table 2 Selected bond lengths (Å) and angles (°) of complex **3**

Structure A		Structure B	
Os(01)–C(3)	1.75(2)	Os(02)–C(7)	1.73(2)
Os(01)–C(4)	1.96(2)	Os(02)–C(6)	2.04(2)
Os(01)–C(5)	2.09(2)	Os(02)–C(9)	2.08(2)
Os(01)–I(003)	2.801(2)	Os(02)–I(004)	2.806(2)
N(1)–C(17)	1.42(2)	N(2)–C(25)	1.45(3)
N(1)–C(4)	1.22(2)	N(2)–C(6)	1.13(2)
O(1)–C(3)	1.19(3)	O(3)–C(7)	1.24(3)
O(2)–C(5)	1.22(2)	O(4)–C(9)	1.24(2)
C(5)–C(14)	1.43(3)	C(9)–C(8)	1.53(3)
C(5)–Os(01)–I(003)	178.4(8)	C(7)–Os(02)–I(004)	177.9(8)
C(4)–Os(01)–C(5)	177.3(7)	C(6)–Os(02)–C(9)	176.1(7)
P(007)–Os(01)–P(008)	175.4(2)	P(005)–Os(02)–P(006)	174.3(2)
N(1)–C(4)–Os(01)	178(2)	N(2)–C(6)–Os(2)	179(2)

cyclohexyl moiety. The Os–I, Os–COMe and Os–P bond lengths in molecules **A** and **B** are the same within the limits of experimental error. On the contrary, while the bond lengths of Os(01)–N(1) and Os(02)–N(2) are the same, the Os(01)–C(4) and C(4)–N(1) single bonds are appreciably different from the Os(02)–C(6) and C(6)–N(2) bonds. The overall symmetry of complex **3** is octahedral with two phosphine ligands occupying two *trans* positions (P–Os–P 175°). The other four ligands (I, COMe, CNC_6H_{11}, CO) lie in the same plane with CNC_6H_{11} *trans* to the COMe group. The relative position of the CNC_6H_{11} nucleophile is common in octahedral structures and is due to the strong *trans* effect of the COMe ligand as observed in many other complexes of iron and ruthenium.[8,23,24]

Structure of complex 1t and comparison of NMR data for 1c and 1t for the triad Fe, Ru and Os

Complex **1t**, reported here for the first time, was synthesized by photochemical isomerization of **1c**. It was not possible to obtain it pure, therefore it was characterized only spectroscopically. In the IR spectrum it shows two CO stretching modes at 2020vw and 1945vs cm^{-1} (hexane) consistent with two CO ligands in *trans* position. The ^1H NMR spectrum in CD_2Cl_2 shows a 'deceptive' triplet[16] at δ 1.34 ($|^2J_{PH} + {}^4J_{PH}| = 3.8$ Hz) indicating that the two PMe_3 ligands are magnetically equivalent and, having the two CO in *trans* position, this means that the two phosphines also have to be *trans*. The remaining ligands Me (observed in the ^1H NMR spectrum at δ 0.25) and the iodide must be *trans* to each other.

It is interesting to compare the ^1H NMR spectra of *cis*, *trans*-$[M(CO)_2(PMe_3)_2(Me)I]$ (**c**) and *trans*,*trans*-$[M(CO)_2(PMe_3)_2(Me)I]$ (**t**) (M = Fe, Ru or Os) complexes in order to identify the spectroscopic parameters characteristic of the structure. The values of δ_{CH_3} and $^3J_{PH}$ are given in Table 3. The CH_3 group in the '**c**' complexes is less shielded than in the '**t**' complexes: the difference in the shielding of the two structures decreases in the order Fe ⩾ Ru ≈ Os. For the complexes having the '**t**' structure the shielding decreases in the series Os > Ru > Fe.[25] Anyway, the values of the chemical shifts are not indicative of the structure. Instead it is interesting that the coupling constants $^3J_{PH}$ are almost independent of the nature of the metal, but depend on the structure of the complex:[26] in fact, in the '**c**' structure $^3J_{PH}$ is in the range 8–9.5 Hz while for the '**t**' structure $^3J_{PH}$ is in the range 4.9–5.9 Hz; therefore these coupling constants are diagnostic of the structure. The different values of $^3J_{PH}$ may be due to the effect of the ligand *trans* to the methyl group:[23] in the '**t**' structures the ligand *trans* to the methyl is I which has higher σ-electron-withdrawing power than CO (*trans* to '**c**') and, consequently, weakens the Os–Me bond more than CO. The coupling constants *J*, which are roughly considered to depend on the electron-density 'transmission', are higher for structure '**c**' having a stronger Os–Me bond.

Table 3 Proton NMR data for *cis*,*trans*-$[M(CO)_2(PMe_3)_2(Me)I]$ (**c**) and *trans*,*trans*-$[M(CO)_2(PMe_3)_2(Me)I]$ (**t**) (M = Fe, Ru or Os)

	Complex **c**		Complex **t**	
M	δ_{CH_3}	$^3J_{PH}$/Hz	δ_{CH_3}	$^3J_{PH}$/Hz
Fe	0.58	9.5	−0.97	5.9
Ru	0.01	8.0	−0.23	5.3
Os	0.52	8.6	0.25	4.9

Thermodynamic results

The equilibrium constants for the reaction of complex **1c** with carbon monoxide (Table 6) are smaller than the corresponding values for the isoelectronic complexes of ruthenium and iron: K_e(Os) = 71.4(4.6), K_e(Ru) = 231(21) (ref. 27) and K_e(Fe) = 1454(85) $dm^3\ mol^{-1}$ (ref. 15) (at 20 °C in toluene). This trend follows that of the enthalpies of the carbonylation reaction: ΔH_e(Os) = −32(2) (Table 6), ΔH_e(Ru) = −42(6.5) (ref. 27) and ΔH_e(Fe) = −47(4) kJ mol^{-1} (ref. 15). Since the entropy variation is nearly the same in the series, both trends are due to the M–R bond strength,[28] which increases for the same group from the first transition series (Fe) to the second (Ru) and to the third (Os).[29]

Reaction mechanism

The pseudo-first-order rate constants for the forward reaction (k_{fwd}) between complex **1c** and carbon monoxide at various temperatures in toluene are given in Table 4, and those for the reaction between **1c** and cyclohexyl isocyanide in toluene at various temperatures are given in Table 5. A summary of the kinetic, thermodynamic and activation results for the reaction between **1c** and carbon monoxide or cyclohexyl isocyanide is given in Table 6.

Table 4 Kinetic results (k_{fwd}) for the carbonylation of complex **1c** with carbon monoxide in toluene at various temperatures

T/°C	10^3[**1c**]/ mol dm^{-3}	P_{CO}/ atm	10^3[CO]/ mol dm^{-3}	$10^6 k_{fwd}$/ s^{-1}	$10^4 k_{CO}$/dm^3 mol^{-1} s^{-1}
10.0	11.40	1	7.99	1.75	2.19
	11.40	1	7.99	1.82	2.28
	8.47	0.50	3.99	0.90	2.26
	8.67	0.35	2.79	0.71	2.54
	8.67	0.35	2.79	0.70	2.51
20.0	16.53	1	7.08	6.13	8.66
	15.69	0.60	4.25	3.53	8.31
	15.74	0.50	3.54	2.50	7.06
	9.80	0.50	3.54	2.38	6.72
	12.42	0.50	3.54	1.66	7.83
30.0	12.23	1	6.29	12.7	20.02
	12.82	1	6.29	14.4	22.89
	10.91	1	6.29	13.6	21.62
	9.65	0.50	3.14	7.47	23.38
	10.77	0.50	3.14	7.98	25.41
	10.52	0.35	2.20	5.35	24.32
	14.08	0.35	2.20	4.72	21.45

Table 5 Pseudo-first-order rate constants (k_{obs}) for the reaction of complex **1c** and cyclohexyl isocyanide in toluene at various temperatures

T/°C	10^3[**1c**]/ mol dm^{-3}	10[$C_6H_{11}NC$]/ mol dm^{-3}	$10^4 k_{obs}$/ s^{-1}
10.0	5.38	0.514	0.110
	5.38	0.734	0.121
	5.38	1.247	0.155
	5.38	5.136	0.233
20.0	5.71	3.280	0.735
	5.71	3.280	0.726
	8.58	3.670	0.733
	8.58	3.670	0.729
	5.39	10.07	0.917
	5.39	1.01	0.457
	5.39	0.719	0.392
	5.71	0.547	0.362
	5.71	0.547	0.348
	8.58	1.836	0.595
	8.58	1.836	0.591
30.0	5.02	0.373	0.850
	5.02	0.711	1.250
	5.11	1.168	1.520
	5.11	5.109	2.460
40.0	5.11	0.512	2.920
	4.86	0.731	3.540
	5.01	1.17	4.380
	5.01	5.10	7.160

The pseudo-first-order rate constants for the equilibrium reaction of complex **1c** with carbon monoxide were calculated using equation (1) where D_o, D_e and D_t are the absorbances of

$$\ln \frac{(D_o - D_e)}{(D_t - D_e)} = (k_{fwd} + k_{rev})\, t = k_{fwd} \frac{a}{x_e} t \qquad (1)$$

the CO stretching modes of complex **1c** at times zero, equilibrium and t, respectively, k_{fwd} and k_{rev} the pseudo-first-order rate constants for the forward and reverse reactions, respectively, and a and x_e the initial concentration of **1c** and the equilibrium concentration of **2c**, respectively. The values of k_{fwd} obtained by using the two CO stretching modes differ by <3%.

The pseudo-first-order rate constants (k_{obs}) for the reaction of complex **1c** with cyclohexyl isocyanide were obtained by monitoring the disappearance of the CO stretching mode at 2004 cm^{-1} using equation (2) in which D_o and D_t are the

$$\ln (D_o/D_t) = k_{obs} t \qquad (2)$$

absorbances of the CO stretching mode at 2004 cm^{-1} at times zero and t, respectively.

The k_{fwd} values for the carbonylation reaction of complex **1c** increase with increasing concentrations of CO (Table 4). The second-order rate constants k_{CO}, defined as k_{fwd}/[CO] (Tables 4 and 6), are independent of the concentration of CO in the limits of experimental error (10%), indicating a second-order kinetic law. The k_{obs} values for the reaction of complex **1c** with cyclohexyl isocyanide increase with increasing cyclohexyl isocyanide concentration (Table 5). A plot of $1/k_{obs}$ *vs.* 1/[$C_6H_{11}NC$] is linear (Fig. 2) with a non-zero intercept.

Both the CO and $C_6H_{11}NC$ results can be interpreted on the basis of the methyl migration mechanism (Scheme 1). The first step involves the formation of an unsaturated intermediate (**I**) which subsequently undergoes attack of the nucleophile L. At the end the entering nucleophile L occupies the position *trans* to the 'orienting group' COMe as can be directly observed when L = $C_6H_{11}NC$ from the crystal structure. Another possibility could be the 'ionic' mechanism (Scheme 2), previously observed for the isoelectronic iron complex,[26b,30] involving ionization of the Os–I bond, co-ordination of L with formation of the cationic methyl complexes (**4** or **5**, L = $C_6H_{11}NC$ or CO,[15] respectively) and re-entry of I^-. This hypothesis has to be excluded owing to the difficulty in obtaining complexes **4** and **5** and to the fact that they do not react with I^- to give back **3**.

When L = $C_6H_{11}NC$ the reaction goes to completion and $k_2 \gg k_{-2}$. Under these conditions, on applying the steady-state approximation to the intermediate **I**, the pseudo-first-order rate constant k_{obs} is given by equation (3). Rearranging this gives

$$k_{obs} = k_1 k_2[L]/(k_{-1} + k_2[L]) \qquad (3)$$

equation (4). Plots of $1/k_{obs}$ *vs.* 1/[$C_6H_{11}NC$] are linear (Fig. 2).

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1 k_2[L]} \qquad (4)$$

Table 6 Summary of the kinetic, thermodynamic and activation results for the reaction of complex **1c** with CO and $C_6H_{11}NC$ in toluene[a]

T/°C	$10^4 k_{CO}$[b]/ dm^3 mol^{-1} s^{-1}	K_e[c]/dm^3 mol^{-1}	$10^4 k_1$[d]/s^{-1} (L = $C_6H_{11}NC$)	$10^6 k_{-2}$[e]/s^{-1}	$k_{-1}k_2^{-1}$/mol dm^{-3} L = CO	$k_{-1}k_2^{-1}$/mol dm^{-3} $C_6H_{11}NC$	$k_2(C_6H_{11}NC)$: k_2(CO)
10.0	2.35(0.16)	103.4(6.4)	0.25(0.02)	2.29(0.14)	0.070	0.117	1.67:1
20.0	8.16(1.32)	71.4(4.6)	0.91(0.03)	10.8(1.3)	0.089	0.112	1.26:1
30.0	22.8(1.56)	44.5(2.6)	2.71(0.15)	53.0(4.1)	0.082	0.119	1.45:1
40.0			8.15(0.47)		0.093		

[a] Values in parentheses are standard deviations at 95% confidence limits. [b] $\Delta H_{CO}^{\ddagger} = 81$ (5) kJ mol^{-1}, $\Delta S_{CO}^{\ddagger} = -49$ (16) J K^{-1} mol^{-1}. [c] $\Delta H_e = -32$ (2) kJ mol^{-1}, $\Delta S_e = -74$ (7) J K^{-1} mol^{-1}. [d] $\Delta H_1^{\ddagger} = 82.5$ (5) kJ mol^{-1}, $\Delta S_1^{\ddagger} = -40$ (8) J K^{-1} mol^{-1}. [e] $\Delta H_{-2}^{\ddagger} = 113$ (4) kJ mol^{-1}, $\Delta S_{-2}^{\ddagger} = 45$ (12) J K^{-1} mol^{-1}.

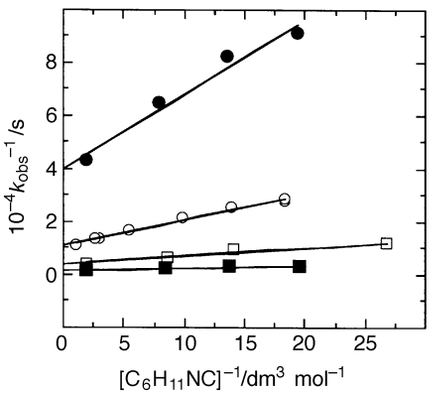
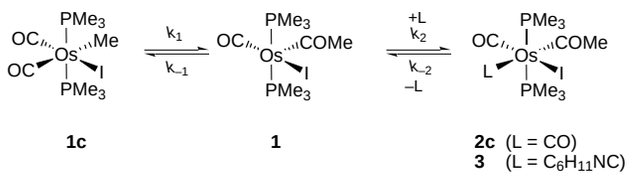
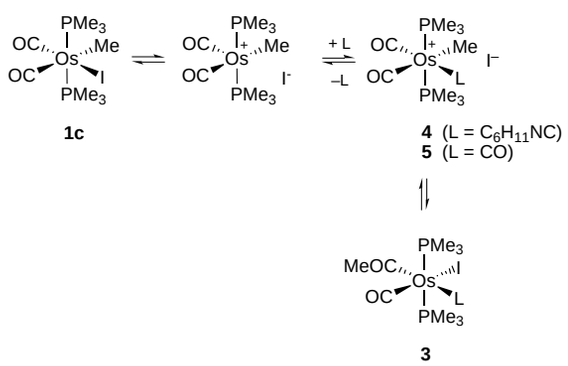


Fig. 2 Plots of $1/k_{obs}$ *vs.* $1/[C_6H_{11}NC]$ for the carbonylation reaction of complex **1c** at various temperatures in toluene: (●) 10, (○) 20, (□) 30 and (■) 40 °C



1c **1** **2c** (L = CO) **3** (L = $C_6H_{11}NC$)

Scheme 1



1c **4** (L = $C_6H_{11}NC$) **5** (L = CO)

3

Scheme 2

The intercept corresponds to $1/k_1$ and k_{-1}/k_2 can be calculated from the slope (Table 6).

When L = CO the reaction does not go to completion but reaches an equilibrium. We have to use equation (1) which gives the k_{fwd} values as a function of the equilibrium parameters. In this case we can still consider equation (3) valid by replacing k_{obs} by k_{fwd}. The k_{fwd} values are a linear function of [CO] only if $k_{-1} \gg k_2[CO]$. Under these conditions $k_{CO} = k_1k_2/k_{-1}$.

On the basis of the mechanism of Scheme 1 the k_1 values are independent of the nature of the L ligand; using the k_1 values obtained with $C_6H_{11}NC$ it is possible to calculate k_{-1}/k_2 also for L = CO from k_{CO} (Table 6). Using the k_{-1}/k_2 values the relative weight of k_{-1} and $k_2[L]$ ($k_{-1}/k_2[L]$) can be evaluated: for L = $C_6H_{11}NC$ the relative weights are in the range 2–0.09 at 20 °C, while for L=CO they are in the range 16–50. This justifies our assumption of a negligible contribution of $k_2[L]$ with respect to k_{-1} in equation (3) for L = CO.

The ratio $k_2(C_6H_{11}NC):k_2(CO)$ (Table 6) gives the relative nucleophilicity of $C_6H_{11}NC$ and CO. These values are close to 1:1 and not influenced by the temperature within the limits of experimental error. The fact that the 'k_2' ratio is close to 1:1 is not surprising because, as observed in many other reactions,[31] unsaturated intermediates show little selectivity toward nucleophiles.

The effect of temperature on the $k_{-1}:k_2$ ratio is negligible; so the effects of temperature on k_{CO} and k_1 should be the same: in fact, within the limits of experimental error, both the activation enthalpies and entropies are the same (Table 6).

From k_{fwd} and K_e it is possible to obtain k_{rev}. In the limits of the experimental errors, k_{rev} is independent of the concentration of CO. Applying the steady-state approximation to the reverse reaction we obtain equation (5). Since $k_{-1} \gg k_2[CO]$, $k_{rev} = k_{-2}$;

$$k_{rev} = k_{-1}k_{-2}/(k_{-1} + k_2[CO]) \quad (5)$$

the k_{-2} values at various temperatures are given in Table 6. The activation enthalpy [$\Delta H_{-2}^{\ddagger} = 113(4)$ kJ mol^{-1}] and entropy [$\Delta S_{-2}^{\ddagger} = 45(12)$ J K^{-1} mol^{-1}] of the reverse reaction are in agreement with the values obtained for the forward reaction and indicate that the rate-determining step of the reverse reaction is dissociation of the CO ligand.

The kinetic results obtained for the osmium complexes can be compared with those obtained for isoelectronic complexes of ruthenium[27] and iron.[30] The reaction rates follow the order Fe < Ru ≫ Os; a direct comparison with iron is not possible owing to the different mechanism; the higher reactivity of the ruthenium complexes (at least 10^4 times) is due to the stronger metal–alkyl bond of the osmium complex.

Conclusion

The most important results of the present work can be summarized as follows.

(1) The carbonylation of the alkyl complexes of osmium is more difficult than that of the isoelectronic complexes of iron and ruthenium and occurs only using CO and $C_6H_{11}NC$ as nucleophiles. This trend can be explained on the basis of the metal–alkyl bond strength.[10] It is not easy to explain why *tert*-butyl isocyanide does not react with complex **1c** even if its different behaviour with respect to cyclohexyl isocyanide has been reported for complexes of other transition metals (for example iron[32]).

(2) The reaction rate for the osmium complexes is at least 10^4 times slower than for the ruthenium;[27] a similar trend was previously observed for iridium and rhodium complexes.[4]

(3) The stereochemistry of the reaction is similar to that observed for ruthenium: the nucleophile enters in *trans* position with respect to the COMe ligand.[8,23,24] Comparison with the iron complexes is not possible because the reaction mechanism is different.[26b,30]

Acknowledgements

This work was supported by grants from the Consiglio Nazionale delle Ricerche (CNR, Rome, Italy) and the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST, Rome, Italy).

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Received 29*th October* 1996; *Paper* 6/07370K