Thermal and Photochemical Behaviour of Organotetraruthenium Clusters: Solution Structures and Dynamics of Phosphine-substituted Derivatives

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The thermal and photochemical behaviour of the organotetraruthenium clusters $[Ru_4(CO)_{12}(PhC_2R)]$ (R = Me or H) and $[Ru_4(CO)_{11}(PhC_2Me)_2]$ is described. Interestingly the reactions of these complexes with phosphorus donor ligands are highly regioselective, as determined by variable-temperature n.m.r. studies. The dynamic behaviour of $[Ru_4(CO)_{10}\{P(OMe)_3\}(PhC_2Me)_2]$ shows for the first time the occurrence of a 'merry-go-round' CO exchange process around the quasi-planar Ru_4 framework.

A considerable part of the research effort in transition metal cluster chemistry has concentrated on the analogy between clusters and surfaces;[1] other studies stress the importance of these compounds as potential homogeneous catalysts[2] due to the occurrence of several adjacent metal centres. However, one snag encountered in the use of transition metal clusters in catalysis is their instability toward thermal and photochemical activation.[3] While this is particularly true for binary carbonyl complexes, *e.g.* $[Ru_3(CO)_{12}]$, organometal clusters[4,5] show an enhancement in stability due to the multicentred interaction between the organic ligand and the metallic framework. On the other hand, the results of Graff and Wrighton[6] indicate that tetranuclear clusters are considerably more stable than the corresponding trinuclear ones towards fragmentation, especially under photochemical activation.

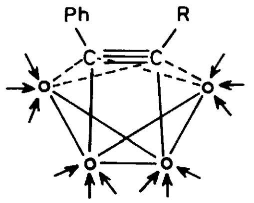
In this paper we compare the thermal and photochemical behaviour, particularly as regards CO substitution reactions, of two tetranuclear organoruthenium clusters, namely $[Ru_4(CO)_{12}(PhC_2R)]$ [R = Me, (**1a**); R = H, (**1b**)] and $[Ru_4(CO)_{11}(PhC_2Me)_2]$ (**2**), containing μ_4-η^2-co-ordinated alkynes. Both complexes (**1a**) and (**2**) are usually formed in the reaction between $[Ru_3(CO)_{12}]$ and internal alkynes;[7] furthermore, the derivative (**1b**) has been obtained in the reaction between $[Ru_3(CO)_{12}]$ with styrene[8] through a dehydrogenation path.

The (**1**) → (**2**) thermal transformation *via* the co-ordination of an additional alkyne molecule has been demonstrated recently.[9]

Experimental

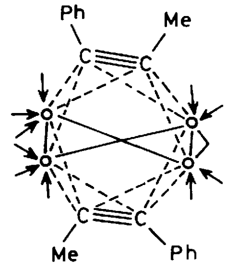
The ruthenium compounds were synthesised as reported in the literature.[7–9] Their purity was checked by mass and i.r. spectroscopy. In order to obtain ^{13}CO-enriched derivatives of (**3a**), (**3b**), and (**5**), for variable-temperature (v.t.) ^{13}C n.m.r. studies, enriched $[Ru_3(CO)_{12}]$ was employed as starting material for their synthesis. The ^{13}CO enrichment was achieved by stirring a solution of $[Ru_3(CO)_{12}]$ in cyclohexane in a sealed ampoule for 4 d at +60 °C in the presence of *ca.* 0.2 atm (2×10^4 N m^{-2}) of ^{13}CO (Monsanto).

U.v.–visible spectra were recorded with a Jasco Uvidec 610 spectrometer. I.r. spectra were obtained with a Perkin-Elmer 283 B spectrometer with a Perkin-Elmer 3600 data station. N.m.r. spectra were recorded with a JEOL JX 270/89 spectrometer; mass spectra with a Kratos AEI MS 12 spectrometer. Elemental analyses were carried out with a F&M model 185 CHN analyser and a Perkin-Elmer 303 atomic absorption spectrophotometer.



(**1a**) R = Me
(**1b**) R = H

o Ru
↗CO



(**2**)

Solvents (Merck grade) were dried by standard procedures. Irradiation was performed using a Hanau medium-pressure mercury lamp equipped with the appropriate filters. Light intensities were determined by ferrioxalate actinometry.[10]

Thin-layer chromatography (t.l.c.) was carried out on commercial Merck plates (coated with a 0.25-mm layer of silica) eluting with n-heptane–diethyl ether (90:10).

Results and Discussion

Quantum Yields for Cluster Disappearance.—The u.v.–visible spectrum of (**1a**) is shown in Figure 1. This spectrum has several bands and shoulders in the visible and near-u.v. at 590 (ε = 530), 530 (ε = 960), 460 (ε = 1 890), 390 (ε = 2 825), and 310 nm (ε = 6 600 dm^3 mol^{-1} cm^{-1}). The spectrum recorded at low temperature [78 K, Figure 1(*b*)] shows a blue shift and a sharpening of the bands at 460 and 390 nm, indicating that these bands are attributable to electronic transitions involving the

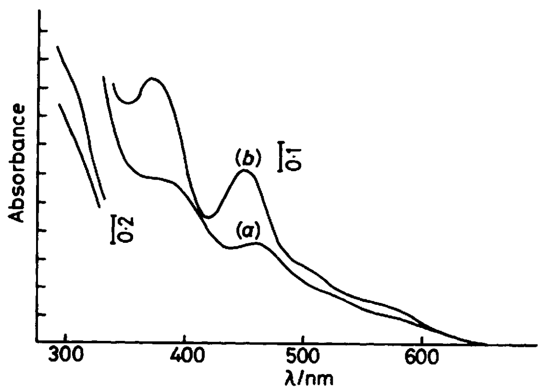


Figure 1. Absorption spectra for $[Ru_4(CO)_{12}(PhC_2Me)]$ in ethyl alcohol (*a*) at 300, (*b*) and 78 K

Table 1. Quantum yields for disappearance of $[Ru_4(CO)_{12}(PhC_2Me)]$

$\lambda_{irr.}$/nm	Saturating atmosphere	Solvent	$\Phi_{dissapp.}$
324	N_2	Heptane	10^{-4}
408	N_2	Heptane	10^{-4}
456	N_2	Heptane	10^{-4}
408	CO	Heptane	$1.3 \times 10^{-3\,a}$
324	N_2	CCl_4	$1.7 \times 10^{-3\,b}$
408	N_2	CCl_4	$7.0 \times 10^{-4\,c}$
456	N_2	CCl_4	$3.8 \times 10^{-3\,c}$

[a] ±0.0005. [b] ±0.0002. [c] 0.000 15.

metal–metal bond.[11] Also apparent is a blue shift of the shoulders at 590 and 530 nm.

The quantum yields for the disappearance of cluster (**1a**) under different experimental conditions are reported in Table 1. For other tetranuclear clusters, *e.g.* $[Ru_4H_4(CO)_{12}]$, the quantum yields for disappearance ($\Phi_{disapp.}$) are quite low in N_2-saturated hydrocarbon solvents. On the other hand, under CO or in CCl_4, an increase in $\Phi_{disapp.}$ is noted, suggesting that the primary photoprocess is the cleavage of a metal–metal bond. It is likely that the product formed in the primary act is a diradical species that does not evolve appreciably towards declusterification in N_2-saturated hydrocarbon solutions. The diradical intermediate may be stabilized by a μ-bridging CO, as suggested by Desrosiers and Ford[12] for $[Ru_3(CO)_{12}]$; certainly in the present case it is further stabilised by the increased number of metal–metal bonds as well as by the 'clasp' effect of the μ_4-η^2-co-ordinated alkyne.

Reaction of (**1a**) *or* (**1b**) *with Phosphorus Donor Ligands.*—Both thermal (n-hexane at reflux, 2 h) and photochemical activation (cyclohexane solution, λ > 400 nm) of a mixture of (**1a**) [or (**1b**)] and PPh_3 afford the monosubstituted derivative $[Ru_4(CO)_{11}(PPh_3)(RC_2R')]$ [R = Me, R′ = Ph, (**3a**); R = H, R′ = Ph, (**3b**)], when the molar ratio is 1:1. At higher concentrations of phosphine ligand, several uncharacterized products are formed, rather than the expected disubstituted derivative.

Under photochemical activation (λ = 408 nm) the substitution reaction to give (**3a**) takes place with a quantum yield of 0.08 ± 0.01. The stoicheiometry and structure of (**3a**) and (**3b**) have been determined conclusively from their analytical and spectroscopic data (Table 2); they are obtained by reaction (1).

$$[Ru_4(CO)_{12}(RC_2R')] + PPh_3 \longrightarrow [Ru_4(CO)_{11}(PPh_3)(RC_2R')] + CO \quad (1)$$

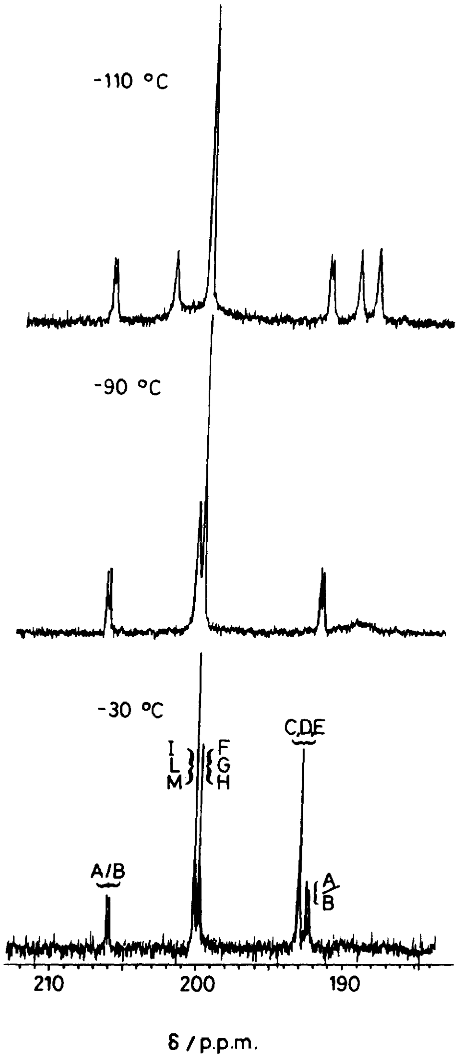
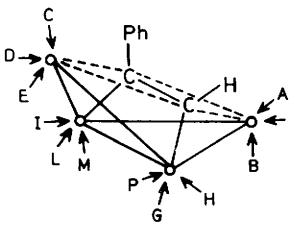


Figure 2. Variable-temperature ^{13}C n.m.r. spectra of $[Ru_4(CO)_{11}(PPh_3)(PhC_2H)]$ (**3b**) recorded at 67.9 MHz in CD_2Cl_2–Freon; the sample was *ca.* 10% ^{13}CO enriched

Inspection of the v.t. ^{13}C n.m.r. spectra provides particularly valuable information on the solution structure and dynamics of these species. At room temperature, (**3a**) shows five resonances in the CO region at 203.5 (J_{PC} = 11.3); 200.4, 200.3, 194.5 (J_{PC} = 13.2 Hz), and 192.6 p.p.m. in the relative intensity ratio 1:3:3:1:3 (solvent, CD_2Cl_2). Analogously (**3b**) exhibits five resonances (relative intensities in parentheses) at 206.2 (1) (J_{PC} = 11.5), 200.3 (3), 199.4 (3) ($^3J_{CH}$ = 1), 193.2 (3), and 192.4 p.p.m. (1) (J_{PC} = 12.1 Hz) [solvent, CD_2Cl_2–Freon (1:1), −30 °C]. The observed coupling pattern and comparison with the spectrum of the unsubstituted parent[8] allow a straightforward assignment of these resonances as shown in Figure 2.

When the temperature is lowered, the signal corresponding to carbonyls C, D, and E broadens (−60 °C), collapses (−80 °C), and gives rise (−110 °C) to three distinct resonances of intensity 1 at 202.8, 190.1, and 188.8 p.p.m. From −80 °C, also the signal corresponding to carbonyls I, L, and M begins to broaden and, at −99 °C, it disappears completely into the baseline. This indicates that the barrier for localized CO exchange on the 'hinge' ruthenium centres is dependent on the nature of the substituents on the alkyne moiety *trans* to them.

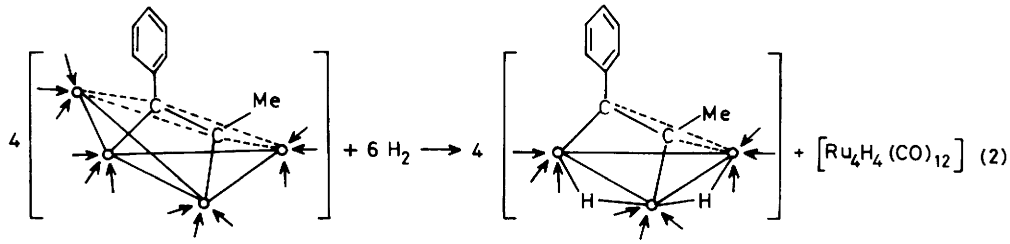


(3b)

These results show that the overall dynamic properties of the parent species[8,13] are maintained in the substituted product, but that the localized CO exchange has been 'frozen out' at the ruthenium unit bearing the phosphine ligand. Furthermore, among the several possible isomers, only one is observed for (**3a**) and (**3b**), indicating that the CO substitution by PPh_3 in these 'butterfly' clusters is regioselective and occurs in the 'wing-tip' position. Similar results are obtained when $P(OMe)_3$ is used instead of PPh_3, affording $[Ru_4(CO)_{11}\{P(OMe)_3\}(PhC_2Me)]$ (**3a′**).

It is worth commenting that the electronic structure of the model butterfly complex $[Ru_4(CO)_{12}(HC_2H)]$ has been obtained by CNDO quantum mechanical calculations.[14] The hinge ruthenium atoms have higher positive electronic charge (because of their strong back-bonding interaction with the alkyne) in respect to their wing counterparts. Thus the substitution of a more basic phosphine ligand for a CO should occur in a hinge position if the process were to be governed by ground-state electronic factors only. This is not the case and it is likely that steric constraints may play a role in this context.

Reaction of (**1a**) *with* H_2.—Irradiation of n-heptane solutions of $[Ru_4(CO)_{12}(PhC_2Me)]$ (**1a**) under H_2 (1 atm) was carried out at different wavelengths, and the reaction course followed by t.l.c. and i.r. spectroscopy. For relatively short irradiation times (<60 min), $[Ru_3H_2(CO)_9(PhC_2Me)]$ (**4**) and $[Ru_4H_4(CO)_{12}]$ are produced according to the overall stoicheiometry in equation (2). Prolonged irradiation led to the formation of $[Ru_4H_4(CO)_{12}]$ and free $PhCH_2CH_2Me$, as previously shown for the exhaustive photolysis of several 1:2 adducts of general formula $[Ru_3H_2(CO)_9(RC_2R')]$.[5] According to the polyhedral skeletal electron pair (p.s.e.p.) approach, developed by Wade and Mingos,[15] the first step in this hydrogenation process is the conversion of the *closo*-octahedron $[Ru_4(CO)_{12}(RC_2R')]$ ($S = 7, n = 6$) to the *nido*-octahedron $[Ru_3H_2(CO)_9(RC_2R')]$ ($S = 7, n = 5$) (S = skeletal electron pairs, n = skeletal atoms) through the loss of '$Ru(CO)_3$' fragments which successively, in the presence of hydrogen, build up the stable $[Ru_4H_4(CO)_{12}]$ hydrido cluster.



As far as the hydrogenation of organometallic ruthenium clusters is concerned, the photoactivation affords clean reactions, in which the hydrido organometallic intermediates can be isolated; on the contrary the thermal process gives directly $[Ru_4H_4(CO)_{12}]$ with the release of the organic chain as alkene or alkane, *e.g.* the hydrogenation of $[Ru_4(CO)_{12}(PhC_2Ph)]$ in n-heptane under reflux gave rise to an almost quantitative yield of $[Ru_4H_4(CO)_{12}]$ and *trans*-stilbene within a few minutes.[7]

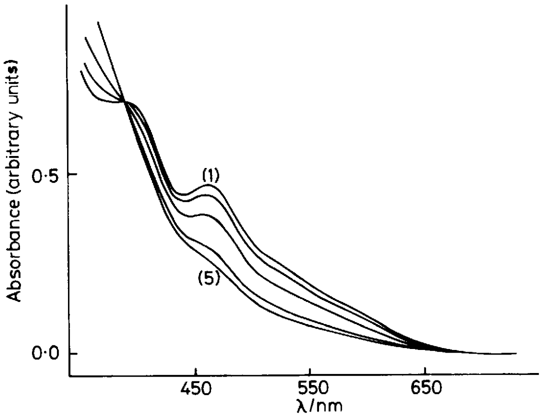


Figure 3. Spectral variation following irradiation (λ = 400 nm) of $[Ru_4(CO)_{12}(PhC_2Me)]$ in n-heptane with an excess of PhC≡CMe: (1) initial spectrum, (5) after 150 min irradiation

Photolysis of (**1a**) *in the Presence of* PhC≡CMe.—Irradiation of a N_2-saturated hydrocarbon solution of $[Ru_4(CO)_{12}(PhC_2Me)]$ (**1a**) containing an excess of PhC_2Me was carried out at different wavelengths, monitoring the reaction by i.r. and u.v.–visible spectroscopy. Typical spectral variations obtained with the latter techniques are shown in Figure 3. An isosbestic point is present at 387 nm which is maintained up to irradiation times of more than 90 min; this indicates a substantially clean transformation of (**1a**) into one product only whose spectroscopic data unambiguously show it to be $[Ru_4(CO)_{11}(PhC_2Me)_2]$ (**2**). The quantum yield for the transformation (**1a**) $\longrightarrow$ (**2**) is *ca.* 10^{-2}. This photochemical behaviour parallels that observed by thermal activation.[9]

Reaction of (**2**) *with Group 5 Donor Ligands*.—The replacement of CO with $P(OMe)_3$ on $[Ru_4(CO)_{11}(PhC_2Me)_2]$ (**2**) occurs quite readily in refluxing n-hexane (2 h) affording $[Ru_4(CO)_{10}\{P(OMe)_3\}(PhC_2Me)_2]$ (**5**) in relatively good yields. Similarly, irradiation of a cyclohexane solution of (**2**) (λ > 400 nm) in the presence of $P(OMe)_3$ led to rapid CO substitution (within 90 s, under experimental conditions), as detected by i.r. spectroscopy. The i.r. bands of the monosubstituted derivative of (**2**) disappeared after irradiation times >3 min; however, no indication of disubstituted compound formation was found.

The ^1H n.m.r. spectrum of (**5**) shows, at room temperature, two doublets for the methyl resonances of the co-ordinated alkyne ligands; the fact that this pattern remains unaltered up to 100 °C clearly demonstrates that the two alkyne molecules are not involved in any rearrangement process across the quasi-planar Ru_4 framework. This behaviour contrasts with the observation of alkyne rotation on the surface of trimetallic clusters {*e.g.* $[M_3H_2(CO)_9(RC_2R)]$ (M = Os or Ru)[16] and

Table 2. Analytical and spectroscopic data for complexes (3)—(5)

	Analysis[a] (%)				
Compound	C	H	Ru	I.r.[b] (ν_{CO}/ cm^{-1})	^{1}H N.m.r.[c] (δ/p.p.m.)
(**3a**) $[Ru_4(CO)_{11}(PPh_3)(PhC_2Me)]$	41.5 (41.85)	2.1 (2.1)	36.9 (37.05)	2 076m, 2 044vs, 2 027vs, 2 019m, 2 000w, 1 985w, 1 962w	7.20—7.55 (m, 20 H), 2.97 (d, 3 H, H,$^4J_{P-H}$ = 3.7)
(**3a′**) $[Ru_4(CO)_{11}\{P(OMe)_3\}(PhC_2Me)]$	29.2 (29.0)	1.8 (1.8)	42.1 (42.45)	2 079m, 2 043vs, 2 028s, 2 013m, 1 997w, 1 984w, 1 960w	7.15—7.60 (m, 5 H), 3.62 (d, 9 H, $^3J_{P-H}$ = 11.5), 3.39 (d, 3 H, $^4J_{P-H}$ = 3.2)
(**3b**) $[Ru_4(CO)_{11}(PPh_3)(PhC_2H)]$	41.4 (41.25)	2.0 (1.95)	37.2 (37.55)	2 076m, 2 039vs, 2 030s, 2 020m, 2 001w, 1 989m, 1 962w	7.05—7.55 (m, 20 H), 9.53 (d, 1 H, $^3J_{P-H}$ = 14.3)
(**4**) $[Ru_3H_2(CO)_9(PhC_2Me)]$[d]	32.5 (32.1)	1.6 (1.5)	44.8 (45.0)	2 105m, 2 078s, 2 055vs, 2 041s, 2 027s, 2 018s, 2 007m, 1 992m	7.01 (m, 5 H), 2.67 (s, 3 H), [e] −15.83 (d, 1 H), −20.41 (d, 1 H), ($^2J_{H-H}$ = 2.0)
(**5**) $[Ru_4(CO)_{10}\{P(OMe)_3\}(PhC_2Me)_2]$	35.9 (35.75)	2.5 (2.4)	38.5 (38.85)	2 062vs, 2 032vs, 2 014s, 1 998m, 1 982m, 1 964w, 1 830w	7.22—6.61 (m, 10 H), 3.84 (d, 9 H, $^3J_{P-H}$ = 12.7), 1.83 (d, 3 H, $^4J_{P-H}$ = 2.3), 1.69 (d, 3 H, $^4J_{P-H}$ = 2.7)

[a] Calculated values given in parentheses. [b] In n-hexane. [c] In $CDCl_3$, *J* values in Hz. [d] Gives clear mass spectrum: *m*/*e* = 676 (M^+). [e] At −60 °C.

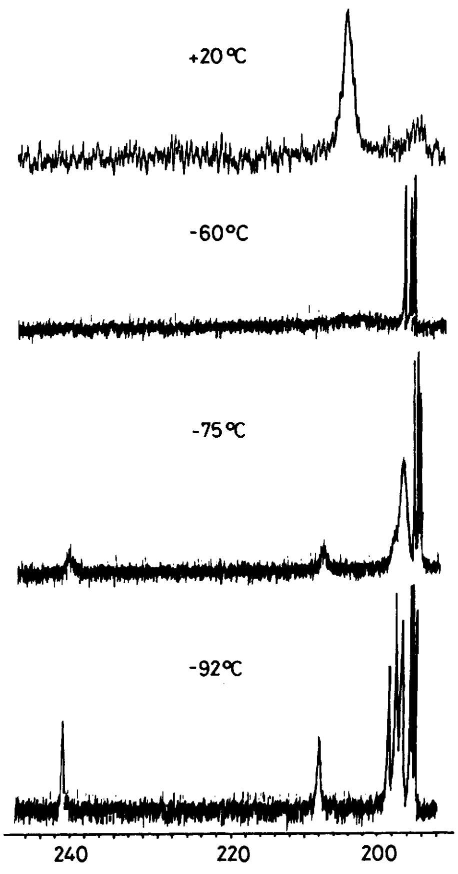
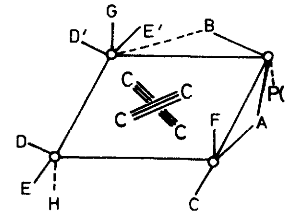


Figure 4. Variable-temperature ^{13}C n.m.r. spectra of $[Ru_4(CO)_{10}\{P(OMe)_3\}(PhC_2Me)_2]$ (**5**) recorded at 67.9 MHz in CD_2Cl_2; the sample was *ca.* 15% ^{13}CO enriched

$[Os_3(CO)_{10}(RC_2R)]$[17]} thus supporting the view that alkyne mobility is facile only in species having a *nido*-polyhedral structure.[18] Actually species (**1**) and (**2**) possess a *closo*-polyhedral skeleton (namely *closo*-octahedron and *closo*-dodecahedron respectively) for which no low-energy path is available for the intramolecular σ→π rearrangement of the alkyne ligand. Interestingly, another alkyne derivative having a *closo* structure, *i.e.* the *closo*-trigonal bipyramid $[Fe_3(CO)_9(RC_2R')]$, does not show any mobility of the RC_2R' moiety on the n.m.r. time-scale.[19]



(**5**)

The substitution of a CO group by $P(OMe)_3$ increases the activation energy barrier for the CO intramolecular exchange processes, and allows, in turn, a satisfactory description of the dynamic behaviour of this type of molecule.

At −92 °C in the spectrum of $[Ru_4(CO)_{10}\{P(OMe)_3\}(PhC_2Me)_2]$ (Figure 4), in the CO region, eight signals are observed respectively at 243.2 (1), 208.2 (1), 198.7 (1), 197.8 (2), 196.9 (2), 195.7 (1), 195.4 (1), and 195.0 p.p.m. (1). As the temperature is increased, the five low-field resonances broaden (−75 °C), disappear (−60 °C), and finally merge into a single resonance at 205.0 p.p.m. (0 °C). Over the same range of temperature, the three upfield signals remain sharp, only at higher temperature (+20 °C) they start to be involved in exchange processes with the other set of CO ligands. Assuming that the relevant structural features, as determined for (**2**) by *X*-ray investigation,[9] are maintained in its $P(OMe)_3$-substituted product (**5**), the observed behaviour suggests that $P(OMe)_3$ occupies an axial position while the other three axial sites are occupied by the carbonyls H, F, and G whose resonances are observed at 195.7, 195.4, and 195.0 p.p.m. respectively. The μ-bridging carbonyl A is easily assigned to the resonance at 243.2 p.p.m. while the resonances of intensity 2 at 197.8 and 196.9 p.p.m. can be attributed to the unresolved resonances due to the radial carbonyls E,E′ and D,D′ and the remaining one at 198.7 (1) p.p.m. to the unique radial carbonyl C. The signal at 208.2 p.p.m. corresponds to a semi-bridging carbonyl (B) which is likely to be bonded to the ruthenium atom bearing the phosphite ligand, and whose occurrence can be accounted for in terms of its ability to equilibrate unequal charge distribution.[20]

The low-energy CO exchange process corresponds then to a 'merry-go-round' process involving all the CO ligands occupying radial co-ordination sites around the quasi-planar Ru_4 framework. This type of process has been reported to occur in several trimetallic derivatives but this is the first direct observation on square-planar cluster complexes.

At higher temperature carbonyls F, G, and H become stereochemically non-rigid, and in the upper temperature range a complete scrambling of all the CO groups is observed. As remarked above for species **(3a)** and **(3b)**, also in this case the CO substitution by a Group 5 donor ligand is regio- and, furthermore, stereo-selective.

Acknowledgements

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