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Triruthenium cluster complexes of C_{60} and C_{70}: carbonyl site exchange probed via triphenylphosphine ligand derivatives

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Abstract

Carbon NMR data obtained for the fullerene complexes $Ru_3(CO)_9(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{60})$ (**1**) and $Ru_3(CO)_9(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{70})$ (**2**) suggest the operation of fluxional processes. Triphenylphosphine-substituted derivatives of **1** and **2** have been prepared by heating the fullerene complex with PPh_3 in chlorobenzene at 130°C for a brief period. The individual mono- and disubstituted derivatives have been purified by thin-layer chromatography and identified by their infrared and FAB mass spectra, and their dynamic behavior has been probed by ^{31}P- and ^{13}C-NMR spectroscopy. Restricted three-fold rotations at each metal center are indicated for these derivatives.

Keywords: Fullerene complexes; Carbon-60; Carbon-70; Ruthenium; Cluster; Dynamic NMR

1. Introduction

The fullerenes C_{60} and C_{70} are three-dimensional polyene compounds that offer multiple potential bonding modes toward metal centers [1,2]. We have communicated the preparation and structure of the first hexahapto complex of C_{60}, namely, $Ru_3(CO)_9(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{60})$ (**1**) [3], and have also reported the corresponding complex of C_{70}, $Ru_3(CO)_9(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{70})$ (**2**) [4]. We subsequently extended our efforts to include the preparation and structural characterization of analogous C_{60} complexes face-bonded to pentanuclear (Ru_5C) and hexanuclear (Ru_6C and $PtRu_5C$) frameworks [5]. Park and co-workers have reported the preparation of the face-bonded triosmium–C_{60} complex $Os_3(CO)_9(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{60})$ as well as NMR and crystallographic studies of the derivatives $Os_3(CO)_8(L)(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{60})$ ($L = PMe_3$, PPh_3) [6].

Solution ^{13}C-NMR data collected in the process of characterizing complexes **1** and **2** suggested the operation of fluxional processes [7]. In order to probe the nature of possible carbonyl ligand site-exchange processes, we have prepared triphenylphosphine derivatives of both **1** and **2**, namely, $Ru_3(CO)_{9-n}(PPh_3)_n(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{60})$ ($n = 1$, **1p**; $n = 2$, **1p2**) and $Ru_3(CO)_{9-n}(PPh_3)_n(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{60})$ ($n = 1$, **2p**; $n = 2$, **2p2**). The ^{13}C- and ^{31}P-NMR spectra of these mono- and bis-(triphenylphosphine) derivatives indicate restricted three-fold rotations at each metal center.

2. Results and discussion

2.1. Synthesis and ^{13}C-NMR spectra of $Ru_3(CO)_9(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{60})$ (1) and $Ru_3(CO)_9(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{70})$ (2)

The synthesis of **1** was originally conducted as a heterogeneous reaction in refluxing *n*-hexane, with a yield of 4% based on unrecovered C_{60} (44% recovered) [3]. We subsequently found that the yield can be improved to 16% with essentially no C_{60} recovered by using refluxing chlorobenzene as the reaction medium. The yield of **1** is limited by the formation of an insoluble black precipitate as a major component; this precipitate contains Ru–CO moieties by IR, but otherwise has proved intractable. Similar reaction conditions provide **2** in 18% isolated yield along with a similar black precipitate. In this case there is also a comparable

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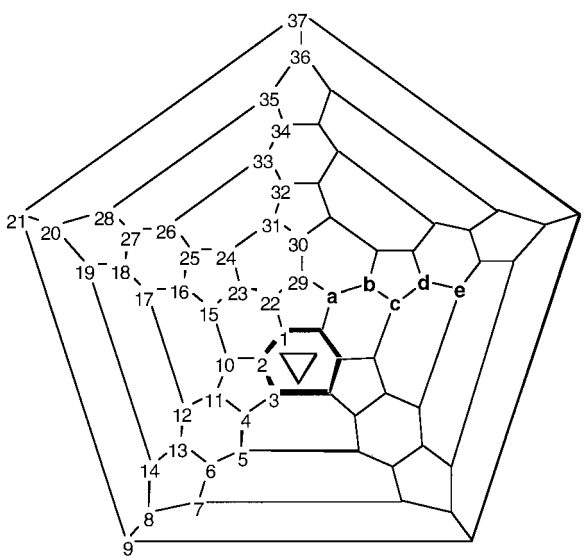
amount of the higher derivative, $\{Ru_3(CO)_9\}_2(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{70})$, which has been shown to be a mixture of three isomers involving coordination of Ru_3 moieties near each pole of the ellipsoidal fullerene. Much smaller amounts of the higher derivatives $\{Ru_3(CO)_9\}_n(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{60})$ ($n = 2$–4) are formed in the case of excess $Ru_3(CO)_{12}$ reacting with C_{60}, and evidence regarding their structures has been discussed elsewhere [7].

For compound **1**, with idealized C_{3v} symmetry, there are 12 types of carbon atoms for the C_{60} moiety, four types correspond to three carbon atoms each and eight types have six carbon atoms each. The $^{13}C\{^1H\}$-NMR spectrum of **1** shows 11 signals in the δ 142–155 ppm region, four with half the intensity of the other seven, which are assigned to the noncoordinated carbon atoms of C_{60}, and a singlet at 73.3 that is assigned to the six coordinated carbon atoms. The upfield shift for the coordinated carbons is clearly due to the change in local hybridization from nearly sp^2 toward sp^3, but this change also lengthens the carbon T1, probably due to diminished chemical shift anisotropy. The result is lower intensity for this signal relative to those for the other C_{60} carbons; increasing the delay time between pulses helped ameliorate the intensity problem, but at the expense of the overall time required for adequate NMR data collection. A singlet at 197.22 is assigned to the nine ruthenium carbonyl ligands, and this assignment was confirmed by preparing a ^{13}CO-enriched sample. Variable-temperature ^{13}C-NMR spectra then showed that the narrow singlet observed at room temperature (r.t.) broadened considerably as the temperature was lowered to -60°C, but no separation of signals was observed. This indicates that the separate axial and equatorial carbonyl ligands are rapidly equilibrated at r.t., but does not differentiate several possible mechanisms. These results for **1** are very similar to those reported for the analogous $Os_3(CO)_9(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{60})$ complex, except that the carbons coordinated directly to the osmium atoms are shifted significantly upfield as expected, i.e. the carbonyls to δ 176.1 and the C_{60}-carbons to δ 61.2 [6a].



Scheme 1.

The ^{13}C-NMR spectrum of C_{70} consists of five signals at δ 150.07 (10C), 147.52 (10C), 146.82 (20C), 144.77 (20C), and 130.28 (10C), corresponding to atom types a, c, b, d and e, respectively [8], as marked on the projection diagram in Scheme 1. As also depicted in Scheme 1, coordination of a Ru_3 triangle to the near-polar C_6 ring (marked in bold) as observed in **2** [4], reduces the idealized symmetry to C_s and leads to the prediction of 37 signals for the carbon atoms of the C_{70} ligand, three @2C for the coordinated C_6 ring, four @1C for the individual carbon atoms in the mirror plane, and 30 @2C for the remainder of the carbon atoms. Indeed, the ^{13}C-NMR spectrum of **2** shows 33 signals in the region δ 132–160, which correspond to 64 carbons, and three signals at δ 71.32, 68.26, and 63.99, which are assigned to the six coordinated carbons. As for **1**, the signals for the coordinated carbons appear less intense. Among the signals for the noncoordinated carbons are four 1C signals at δ 159.69, 154.60, 149.83, and 149.10, which correspond to the four carbons lying on the mirror plane, and a set of four signals at δ 134.79 (2C), 132.57 (2C), 132.22 (4C), 132.10 (2C), which clearly correspond to the five distinct kinds of type e 'equatorial belt' carbons (nos. 5, 12, 17, 26, and 33 in Scheme 1). The range of carbon signals is comparable with those reported for organic adducts of C_{70} [9], and a similar distinct region for the equatorial belt carbons is observed for some isomers.

The ^{13}C-NMR spectrum of **2** at r.t. also shows two singlets in a ratio of 1:2 for the carbonyl carbons. The separate sets are presumably due to the two different types of $Ru(CO)_3$ groups in **2**, assuming rapid local equilibration at each metal center. As shown in Fig. 1, heating the sample causes the two signals to broaden, coalesce and sharpen into a single resonance. Two possibilities for the mechanism of this equilibration include rotation of the coordinated C_6 ring against the Ru_3 framework or internuclear carbonyl scrambling, but the data available for **2** do not discriminate. We therefore turned to the examination of phosphorus ligand derivatives.

2.2. Triphenylphosphine ligand derivatives of *1* and *2*

The interaction between the Ru_3 triangle and C_{60} or C_{70} in **1** or **2** is quite robust; for example, heating a chlorobenzene solution of **1** at 130°C under CO pressure (35 psig) for 5 h caused no decomposition or formation of free C_{60}. Direct phosphine ligand substitution reactions with **1** or **2** can therefore be carried out at high temperatures in good overall yield. The reaction

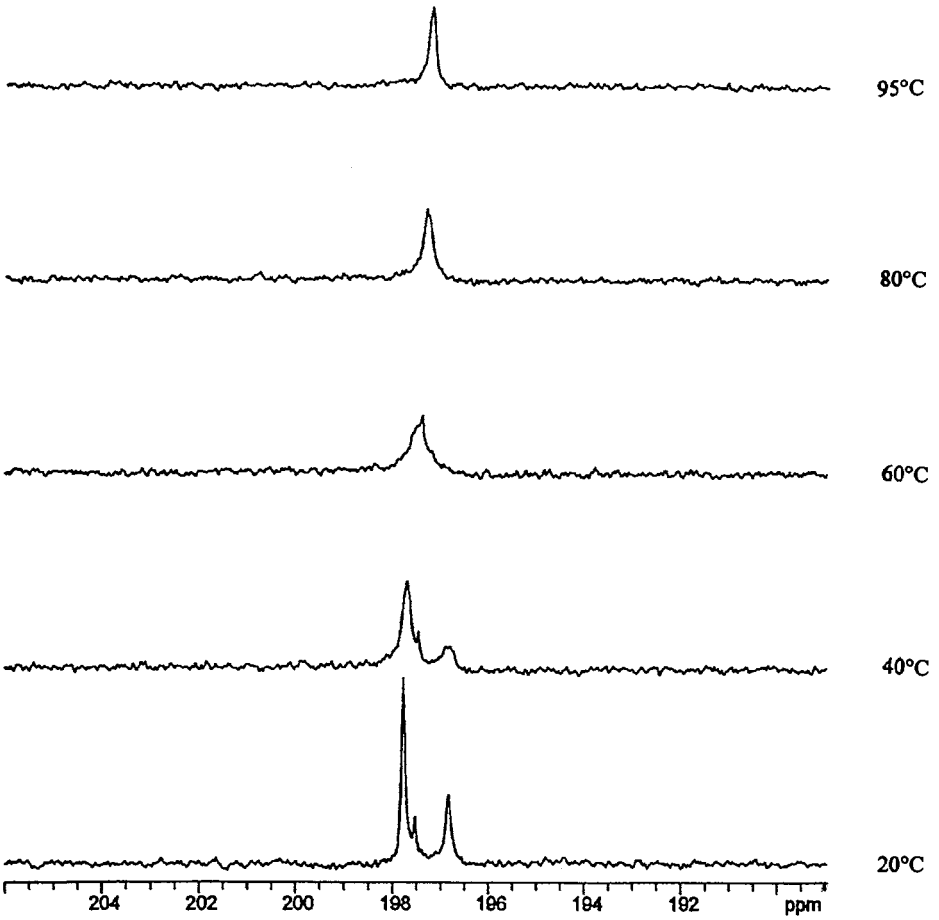


Fig. 1. Carbonyl ^{13}C-NMR spectra of $Ru_3(CO)_9(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{70})$ (**2**). The sharp singlet at 197.6 is due to the presence of a small amount of **1**.

of **1** or **2** with PPh_3 in refluxing chlorobenzene for 5 min provided $Ru_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{60})$ (**1p**, 70%) and $Ru_3(CO)_7(PPh_3)_2(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{60})$ (**1p2**, 8%) or $Ru_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{70})$ (**2p**, 73%), and $Ru_3(CO)_7(PPh_3)_2(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{70})$ (**2p2**, 9%) after TLC separation. The substituted compounds can also be prepared at r.t. or below by adding Me_3NO to a dichloromethane solution of **1** or **2** with PPh_3, but the disubstituted compound is the major product under these circumstances. Upon substitution of the phosphine ligand(s) into **1** or **2**, the carbonyl stretching frequencies expectedly shift to lower energy; the resulting spectra are essentially identical for the monosubstituted pair **1p** and **2p** or the disubstituted pair **1p2** and **2p2**, respectively.

2.3. $^{31}P\{^1H\}$- and $^{13}C\{^1H\}$-NMR spectra of *1p* and *1p2*

The triphenylphosphine ligand is expected to occupy an in-plane (equatorial) coordination site of the Ru_3 triangle in the structure of **1p**, based on known structures of the phosphine ligand derivatives $Ru_3(CO)_{12-n}(L)_n$ [10] and on the structure of the osmium analog $Os_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{60})$ recently reported by Park and co-workers [6b]. A single isomer is then expected for **1p**, and the $^{31}P\{^1H\}$-NMR spectrum consists of one singlet at 37.7 ppm. However, the $^{13}C\{^1H\}$-NMR spectrum of ^{13}CO-enriched **1p** shows a 2C doublet at δ 206.3 ($J = 7$ Hz) and a 6C singlet at δ 199.3 (Fig. 2(A)). The doublet signal is assigned to the two carbonyl ligands on the substituted Ru atom, with coupling to the phosphorus nucleus. The observation of individual carbonyl signals in a ratio of 2:6, corresponding to the sets of carbonyls on the two types of ruthenium atoms in **1p**, rules out internuclear migration pathways for CO equilibration and indicates that the carbonyl ligands are locally equilibrated on each metal center. The diagrams in Scheme 2 show specifically how restricted three-fold rotation at the substituted Ru center can lead to equilibration of the distinct axial and equatorial carbonyl ligands. A similar spectrum and interpretation was reported for the case of $Os_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{60})$ [6].

We have determined the crystal structure of **1p2** by X-ray crystallography, and the details are discussed elsewhere [7]. The important qualitative result revealed by this study was that each phosphorus ligand not only adopted an equatorial position at separate Ru atoms, as expected [10], but also that the ligands were in

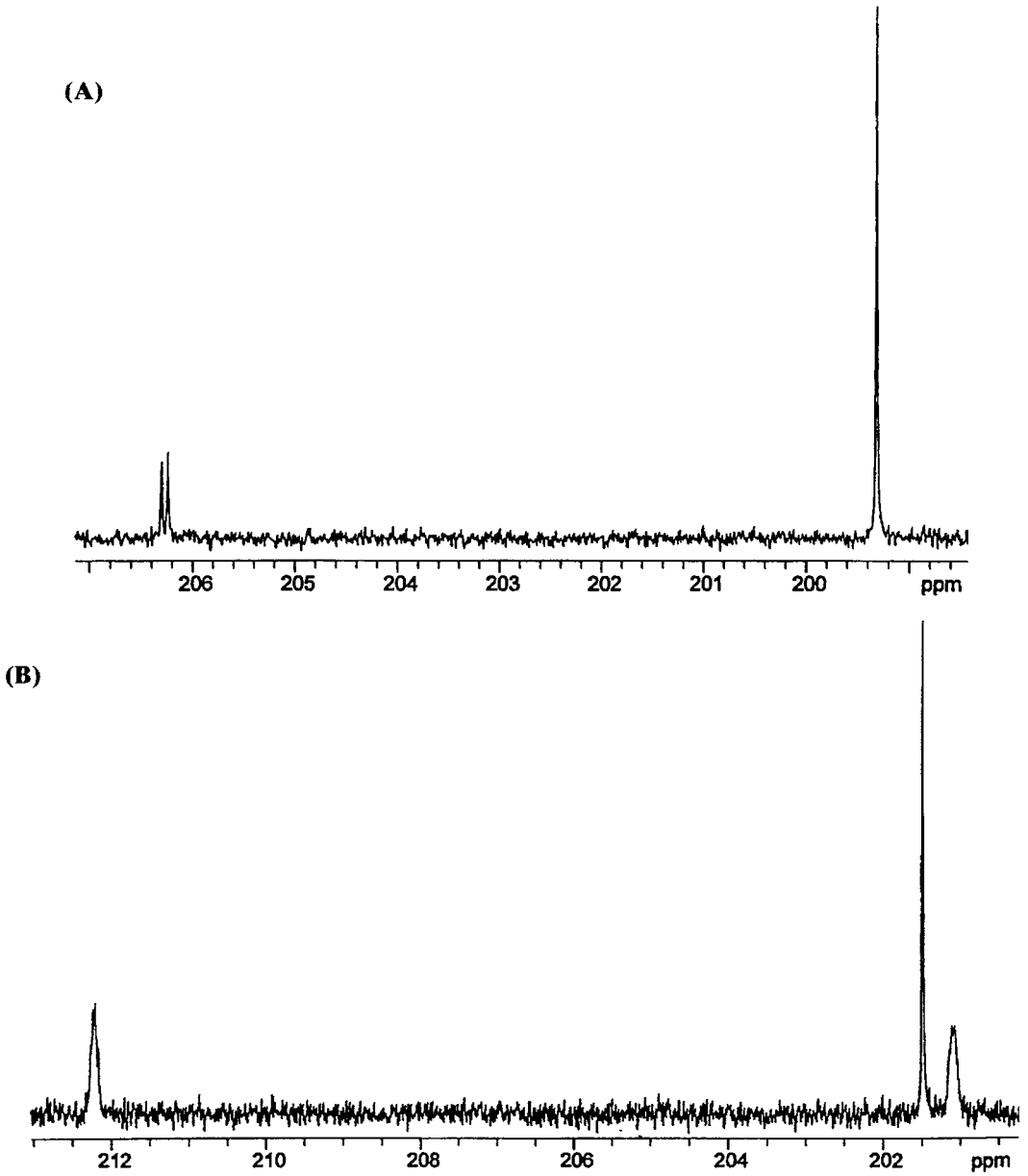
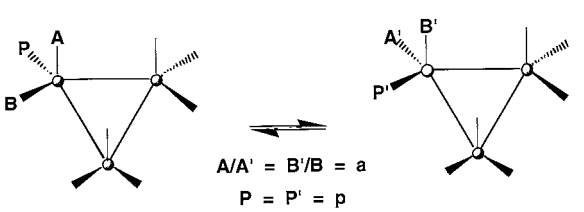
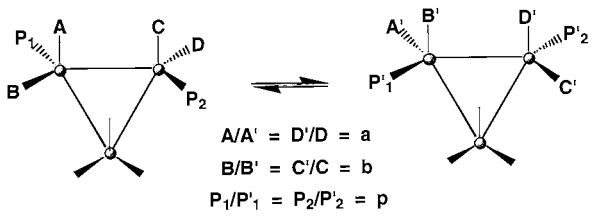


Fig. 2. Carbonyl ^{13}C-NMR spectra of (A) $Ru_3(^{13}CO)_8(PPh_3)(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{60})$ (**1p**) and (B) $Ru_3(^{13}CO)_7(PPh_3)_2(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{60})$ (**1p2**).

chemically inequivalent positions. However, only one ^{31}P-NMR signal at 41.3 ppm is observed for **1p2** in solution, implying either rearrangement to a symmetrical isomer or a dynamic process equilibrating the distinct phosphine ligand sites. The $^{13}C\{^1H\}$-NMR spectrum of ^{13}CO-enriched **1p2** supports the latter interpretation. As shown in Fig. 2(B), three peaks in a ratio of 2:3:2 are observed. The sharp singlet is assigned to the three carbonyl ligands on the unsubstituted ruthenium center, and the two broad multiplets are assigned to two pairs of inequivalent carbonyl ligands, which are each coupled to two magnetically inequivalent phosphorus nuclei. The diagrams in Scheme 3 show that this result can be explained by the exchange via restricted three-fold rotations of an axial carbonyl on one substituted Ru center (e.g. **A**) with an equatorial carbonyl on the adjacent substituted Ru center (e.g. **D**) and vice versa, but the two carbonyls on each of the Ru centers remain diastereotopic and do not equilibrate. The three-fold rotations do interchange the two phosphorus



Scheme 2.



Scheme 3.

ligands, thereby leading to the single ^{31}P signal observed. We surmise that the distinctly different average chemical shift values for the two carbonyl signals **a** and **b** are determined by different relationships with the average orientations of the phenyl groups of the triphenylphosphine ligands.

2.4. $^{31}P\{^1H\}$- and $^{13}C\{^1H\}$-NMR spectra of **2p** and **2p2**

The $^{31}P\{^1H\}$-NMR spectrum of **2p** shows two singlets at 37.9 and 36.5 ppm, with a ratio of 2:1 (Fig. 3(A)). This would appear to correspond to substitution of a ligand on each of the two possible Ru centers (ratio 2:1) in the C_s symmetric structure of **2**. However, since there are two distinct equatorial substitution sites at each major center, local equilibration is implied.

The $^{13}C\{^1H\}$-NMR spectrum of ^{13}CO-enriched **2p** is shown in Fig. 4, and the assignments are indicated in Scheme 4. Three large singlets in the spectrum correspond to the individual $Ru(CO)_3$ groups, two equivalent ones in the minor isomer and two inequivalent ones in the major isomer. The clean doublet at δ 204.76 ($J_{PC} = 7.6$ Hz) is due to equilibration of the two carbonyls on the substituted Ru center of the minor iso-

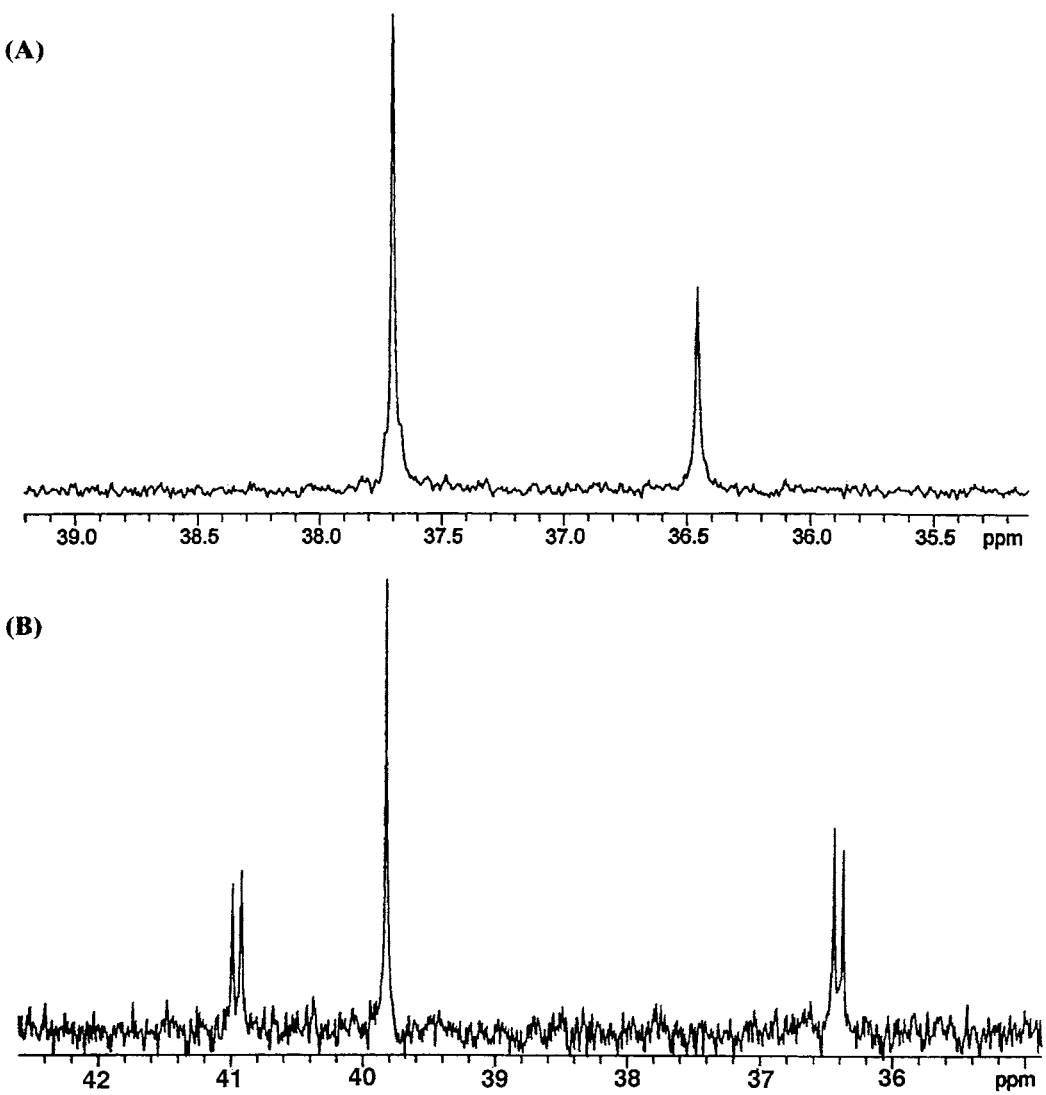


Fig. 3. ^{31}P NMR spectra of (A) **2p** and (B) **2p2**.

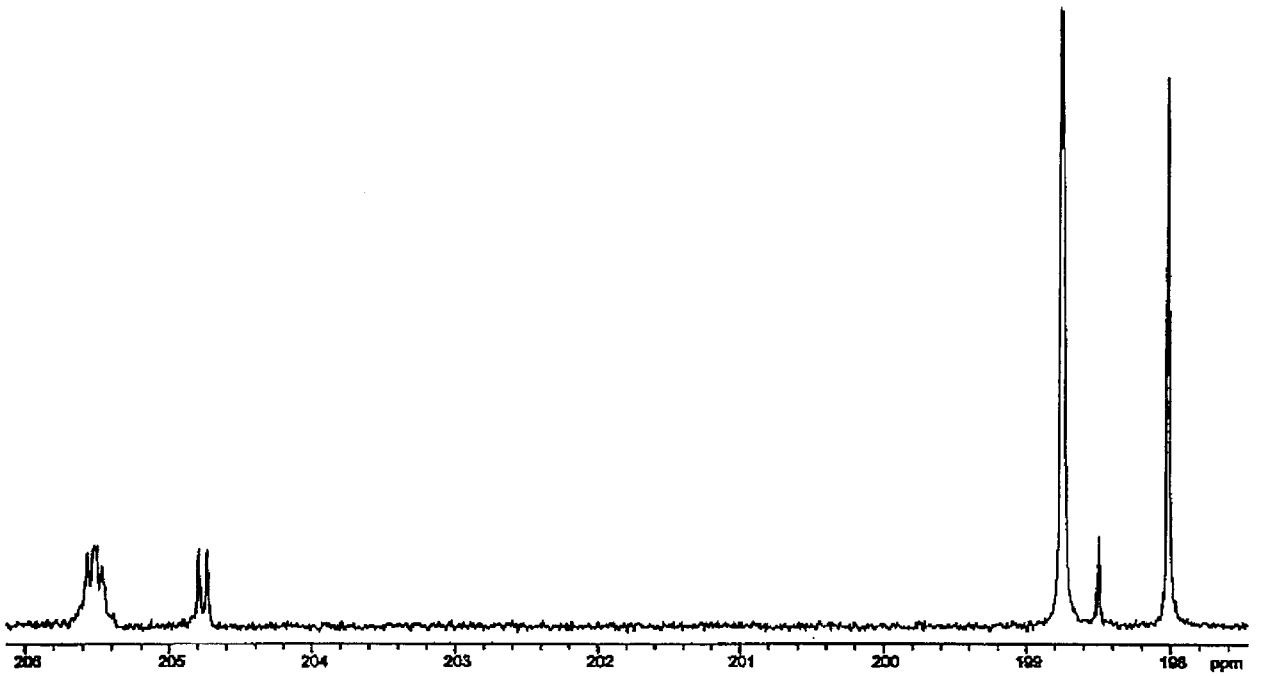


Fig. 4. Carbonyl ^{13}C-NMR spectra of **2p**.

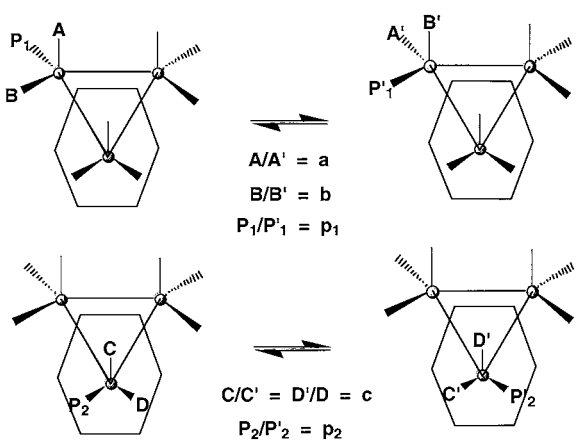
mer; this situation is completely analogous to that discussed above for **1p**. The multiplet at δ 205.54 is an AB multiplet with superimposed ^{31}P coupling due to the two carbonyls on the substituted Ru center of the major isomer. In this case local three-fold rotation does not fully equilibrate these two carbonyls, and they maintain two separate, closely spaced signals.

The ^{31}P{^{1}H}-NMR spectrum of **2p2** (Fig. 3(B)) also suggests the operation of a local equilibration process. A singlet at 39.86 ppm corresponds to equivalent substitution at each of the major Ru centers, and a pair of doublets at 40.99 and 36.44 ppm (with $J_{PP} = 11$ Hz) is due to inequivalent substitution at one major and one minor Ru center. The ratio of the symmetric form to the unsymmetrical form is ca. 2:3.

The ^{13}C{^{1}H}-NMR spectrum of ^{13}CO-enriched **2p2** is shown in Fig. 5, and the assignments are indicated in Scheme 5. The ^{13}C-NMR resonances can be divided into two groups based on their integration intensities, with an overall ratio of 2:3. The first group consists of two broad peaks (**a**, **b**) and one sharp singlet in a ratio of 2:2:3. These signals correspond to the symmetric form seen in the ^{31}P-NMR spectrum, and the spectral pattern is analogous to that seen for **1p2** in Fig. 2(B). The second group of signals consists of three broad peaks and one singlet in a ratio of 1:1:2:3 for the unsymmetrical form. The singlet is due to the unsubstituted $Ru(CO)_3$ center, and the remaining four signals are for the two pairs of carbonyls on the substituted centers. As shown by the diagrams in Scheme 5, localized three-fold rotations do not fully equilibrate any of these sites, and the separate averaged signals are expected.

2.5. Summary

Our ^{31}P- and ^{13}C-NMR data on the triphenylphosphine derivatives of **1** and **2** are fully consistent with restricted three-fold rotations at each metal center as the dominant dynamic process in each case. The observation of separate signals for the isomers of **2p** and **2p2** indicates that neither internuclear carbonyl migration nor rotation of the C_{70} moiety against the Ru_3 framework is rapid at r.t. Nevertheless, one of these processes may be indicated for unsubstituted **2** by the ^{13}C-NMR behavior observed at higher temperatures.



Scheme 4.

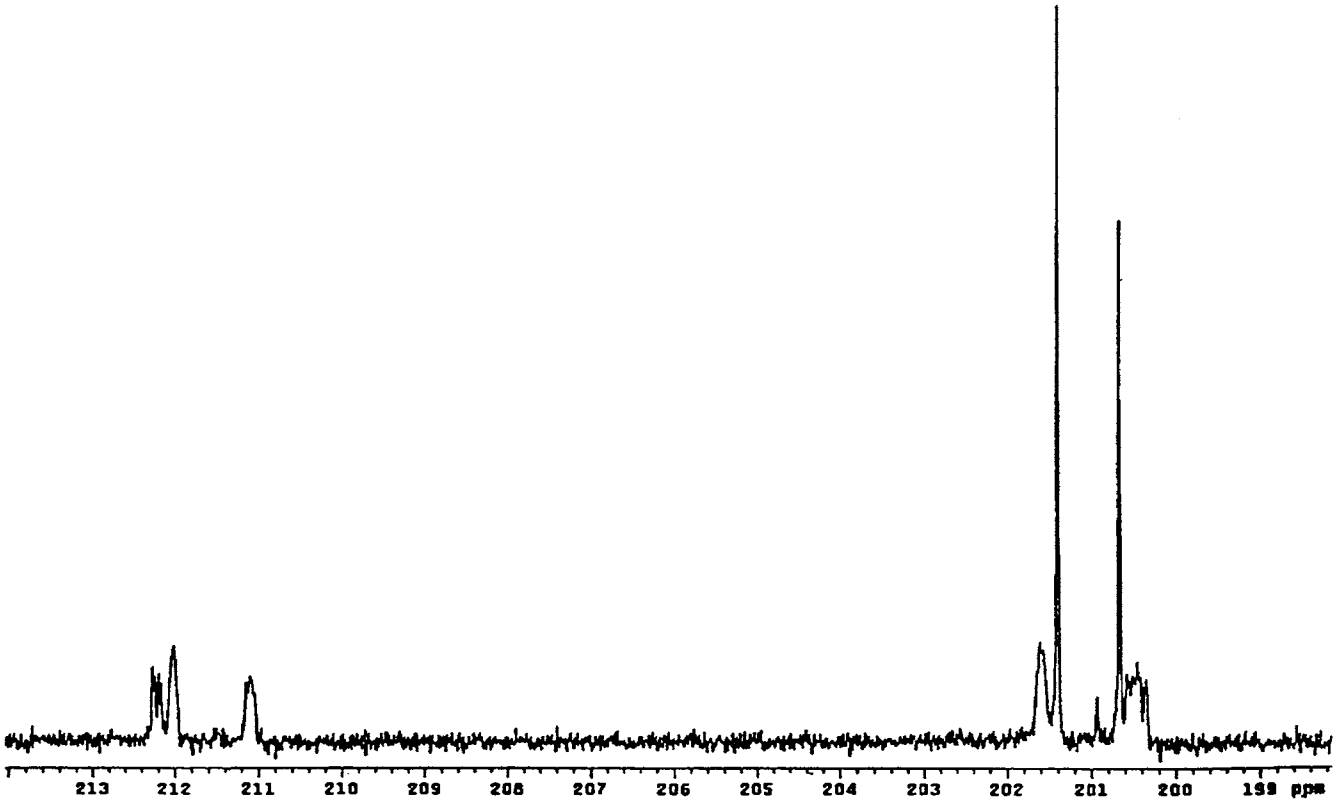


Fig. 5. Carbonyl ^{13}C-NMR spectra of **2p2**.

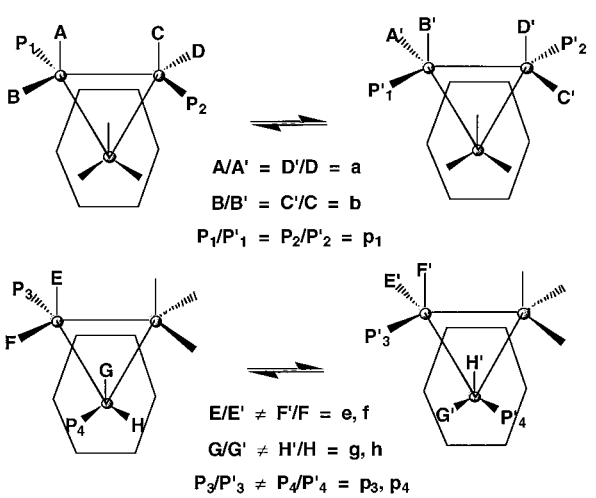
3. Experimental

3.1. General procedures

All reactions were conducted under an atmosphere of nitrogen using standard Schlenk techniques. Separation of products was accomplished by thin-layer chromatography (TLC) using SiO_2 plates (E. Merck, Kieselgel 60 F254, 0.25 mm). Chlorobenzene was distilled under nitrogen from calcium hydride before use. ^{13}C- and ^{31}P-NMR spectra were recorded on a Varian UI500 spectrometer referenced to a solvent resonance (53.8 ppm for CD_2Cl_2) or to an external H_3PO_4 reference for ^{31}P-NMR spectroscopy. Infrared spectra were recorded on a Perkin–Elmer 1750 FTIR spectrometer. Fast atom bombardment (FAB) mass spectra were recorded on a VG ZAB-SE spectrometer and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Micromass TofSpec spectrometer, with a *trans*-3-indoleacrylic acid matrix, by the staff of the Mass Spectrometry Laboratory of the School of Chemical Sciences.

3.2. $Ru_3(CO)_9(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{60})$ (*1*)

A solution of $Ru_3(CO)_{12}$ (50 mg, 0.078 mmol) and C_{60} (50 mg, 0.069 mmol) was heated in chlorobenzene under reflux for 1.5 h until TLC monitoring showed complete use of C_{60}. The solution was dried under vacuum and the residue was extracted with carbon disulfide. The resulting red solution was concentrated to 3 ml and then separated by preparative TLC on several plates with carbon disulfide to yield (in order of elution) unreacted C_{60} (purple, 1 mg) and $Ru_3(CO)_9(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{60})$ (**1**, red, 14 mg, 0.011 mmol, 16% based on C_{60}). IR (CS_2): 2078 (s), 2045 (s), 2012 (m), 1985 (w)



Scheme 5.

cm^{-1}. MALDI-TOF MS: m/z 1276. ^{13}C-NMR (125.7 MHz; at = 1.086 s, pd = 0 s, pw = 10.6 μs, no. acquisitions = 29 996; 1:1 CD_2Cl_2–CS_2): δ 197.2(9), 154.6(6), 149.8(3), 147.8(6), 146.6(6), 145.4(6), 145.3(6), 144.6(6), 144.2(3), 143.5(6), 143.4(3), 142.6(3), 73.27(6).

3.3. $Ru_3(CO)_9(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{70})$ (2)

A chlorobenzene solution of C_{70} (50 mg, 0.060 mmol) was added dropwise to a chlorobenzene solution of $Ru_3(CO)_{12}$ (50 mg, 0.078 mmol) under reflux over a period of 30 min. The solution was further heated for 30 min. The solvent was removed under vacuum, and the residue was separated on TLC (SiO_2, CS_2) to provide **2** (15 mg, 0.011 mmol, 18%) together with a smaller amount of the isomeric mixture of $\{Ru_3(CO)_9\}_2(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{70})$ [4] (7 mg, 0.004 mmol, 7%) in order of elution. $Ru_3(CO)_9(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{70})$ (**2**): MALDI-TOF MS: m/z 1396. IR (CS_2): 2078 (s), 2045 (s), 2011 (m), 1984 (w) cm^{-1}. ^{13}C-NMR (125.7 MHz, at = 1.086 s, pd = 1 s, pw = 10.6 μs, no. acquisitions = 29 996, 1:1 CD_2Cl_2–CS_2): δ 197.26(6), 196.38(3), 159.70(1), 156.40(2), 154.60(1), 152.93(2), 152.18(2), 151.69(2), 150.89(2), 150.82(2), 150.29(2), 149.88(1), 149.84(2), 149.58(2), 149.29(2), 149.07(1), 149.00(1), 148.68(2), 148.04(2), 147.68(2), 147.52(2), 147.33(2), 147.10(2), 146.62(2), 145.98(2), 145.54(2), 144.86(2), 144.51(2), 143.88(2), 142.54(2), 142.52(2), 134.79(2), 132.57(2), 132.22(4), 132.10(2), 71.32(2), 68.26(2), 63.99(2).

3.4. $Ru_3(CO)_{9-n}(PPh_3)_n(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{60})$, $n = 1, 2$

A solution of **1** (15 mg, 0.012 mmol) and PPh_3 (3 mg, 0.011 mmol) in chlorobenzene was heated under reflux for 5 min. The solvent was removed in vacuum, and the residue was separated by TLC, eluting with 1:1 chloroform–*n*-hexane to yield unreacted **1** (< 1 mg), brown **1p** (12 mg, 0.008 mmol, 70%) and brown **1p2** (2 mg, 0.001 mmol, 8%). Black crystals of **1p2** were obtained from 1:1 CS_2–MeOH.

$Ru_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{60})$ (**1p**): FAB(+)-MS: m/z 1512. IR (CH_2Cl_2): ν(CO) 2061 (s), 2032 (m), 2014 (w), 2004 (w, sh),1985 (w), 1960 (w, br) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.3 (m, C_6H_5). ^{31}P{^{1}H}-NMR (MHz, $CDCl_3$): 37.58 ppm. ^{13}C-NMR of ^{13}CO-enriched **1p** (125.7 MHz, $CDCl_3$): δ 206.3 (d, J(C–P) = 7 Hz, 2CO), 199.3 (s, 6CO).

$Ru_3(CO)_7(PPh_3)_2(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{60})$ (**1p2**): FAB(+)-MS: m/z 1746. IR (CH_2Cl_2): ν(CO) 2037 (s), 2014 (s), 1979 (m, br) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.3 (m, C6H5). ^{31}P{^{1}H} NMR (121.6 MHz, $CDCl_3$): 41.32 ppm. ^{13}C-NMR of ^{13}CO-enriched **1p2** (125.7 MHz, $CDCl_3$): δ 212.20 (m, 2CO), 201.49 (s, 3CO), 201.11 (m, 2CO).

3.5. $Ru_3(CO)_{9-n}(PPh_3)_n(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{70})$, $n = 1, 2$

(a) A solution of **2** (15 mg, 0.011 mmol) and triphenylphosphine (3 mg, 0.011 mmol) in chlorobenzene was heated under reflux for 5 min. The solvent was removed in vacuo, and the residue was separated by TLC, eluting with 1:1 chloroform–*n*-hexane to yield brown **2p** (13 mg, 0.008 mmol, 73%) and brown **2p2** (2 mg, 0.001 mmol, 9%).

(b) A solution Me_3NO (1 mg, 0.013 mmol) in dichloromethane was added dropwise over a period of 20 min. to a solution of **2** (15 mg, 0.011 mmol) and triphenylphosphine (3 mg, 0.011 mmol) in dichloromethane at −78°C. The solution was then warmed to r.t. and stirred for 30 min. The solvent was removed under vacuum, and the residue was separated by TLC, eluting with 1:1 chloroform–*n*-hexane to yield **2p** (3 mg, 0.0018 mmol, 16%) and **2p2** (10 mg, 0.0054 mmol, 49%).

$Ru_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{70})$ (**2p**): FAB(+) MS: m/z 1632. IR (CH_2Cl_2): ν(CO) 2061 (s), 2032 (m), 2015 (m), 2004 (w, sh), 1985 (w), 1962 (w, br) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.3 (m, C_6H_5). ^{31}P{^{1}H}-NMR (121.6 MHz, $CDCl_3$): 37.87 (s), 36.45 (s) ppm in a ratio of 2:1. ^{13}C-NMR of ^{13}CO-enriched **2p** (125.7 MHz, $CDCl_3$): δ(CO) 205.54 (m), 204.76 (d, J(C–P) = 7.4 Hz), 198.75 (s), 198.73 (s), 198.01 (s) in a ratio of 2:1:3:3:3.

$Ru_3(CO)_7(PPh_3)_2(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{70})$ (**2p2**): FAB(+) MS: m/z 1866. IR (CH_2Cl_2): ν(CO) 2037 (s), 2013 (s), 1979 (m, br) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.3 (m, C_6H_5). ^{31}P{^{1}H}-NMR (121.6 MHz, $CDCl_3$): 40.99 (d, J(P–P) = 11 Hz), 39.86 (s), and 36.44 (d, J(P–P) = 11 Hz) ppm in a ratio of 1:1.4:1. ^{13}C-NMR of ^{13}CO-enriched **2p2** (125.7 MHz, $CDCl_3$): δ 212.21 (dd, J(C–PA) = 9 Hz, J(C–PB) = 4 Hz), 212.01 (m), 211.08 (m), 201.61 (m), 201.40 (s), 200.66 (s), 200.45 (m) in a ratio of 3:4:3:4:9:6:6.

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