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Journal of Organometallic Chemistry 561 (1998) 97–107

Journal of Organometallic Chemistry

Carbonyl substitution reactions of ruthenium cluster complexes containing dicarbon (C_2) ligands: X-ray structures of $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}(L)$ [$L = CNBu^t$, $P(OMe)_3$]

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Received 27 November 1997

Abstract

Addition of Bu^tNC to $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}$ (**1**) gives $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}(CNBu^t)$ (**3**), in which the Ru_5 pentagon has become flattened, with Ru–Ru separations longer on average by 0.08 Å. On heating, loss of CO restores the cluster geometry in $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}(CNBu^t)$ (**2**) to that of **1**. Reactions between **1** and $MeCN/Me_3NO$ afforded the lightly-stabilised cluster $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}(NCMe)$ (**4**). In a similar manner $Ru_6(\mu_6\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu_3\text{-}SMe)_2(CO)_{14}$ (**5**) yielded $Ru_6(\mu_6\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu_3\text{-}SMe)_2(CO)_{13}(NCMe)$ (**6**). Displacement of MeCN by PPh_3 gave $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}(PR_3)$ [R = OMe (**7**), Ph (**8**)] and $Ru_6(\mu_6\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu_3\text{-}SMe)_2(CO)_{13}(PPh_3)$ (**10**). When **4** and **6** were reacted with dppa [bis(diphenylphosphino)acetylene] the 'dumbell' clusters $\{Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}\}_2(\mu\text{-}dppa)$ (**9**) and $\{Ru_6(\mu_6\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu_3\text{-}SMe)_2(CO)_{14}\}_2(\mu\text{-}dppa)$ (**11**) were formed in high yield. The structure of **7** was determined by X-ray crystallography and showed that substitution occurred at the ruthenium atom attached to the C_2 ligand by the shortest Ru–C bond. Reactions of **1** with *n*-butylamine afforded $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}(NH_2Bu)$ (**12**), but secondary and tertiary amines such as $NHEt_2$ and NEt_3 gave only the previously reported $Ru_5(\mu_5\text{-}CCH_2)(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)_2(CO)_{10}$ (**13**). © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Carbonyl clusters; Dicarbido clusters; Substitution reactions

1. Introduction

We have been interested in the synthesis of metal carbonyl clusters containing all-carbon ligands such as C_2 and C_4 for several years [1]. In the course of these studies, we have devised methods for obtaining complexes such as $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}$ (**1**) [2] and $\{Ru_3(\mu\text{-}PPh_2)(CO)_9\}_2(\mu_3,\mu_3\text{-}C_4)$ [3] in high yield. These interesting compounds have been a rich source of chemistry, which has been summarised elsewhere [1,4]. We have examined some of their simple carbonyl substitution reactions with a view to introducing other functional ligands, and have briefly reported the addition/dissociation reactions that occur between **1** and Bu^tNC, resulting in substitution at the unique Ru atom [5]. We have now extended this work to some related reactions with *N*- and *P*-donor ligands.

In the chemistry of ruthenium cluster carbonyls, a facile route to substituted complexes is by the trimethylamine oxide-induced oxidation of one or two CO ligands [6,7]. Under appropriate conditions, the acetonitrile-substituted complexes may be isolated, but reactions are often carried out in the presence of other ligands, leading to direct preparation of the substituted complexes. We have found that this route is also applicable to our cluster complexes, the reactions often proceeding in high yield, giving products which are

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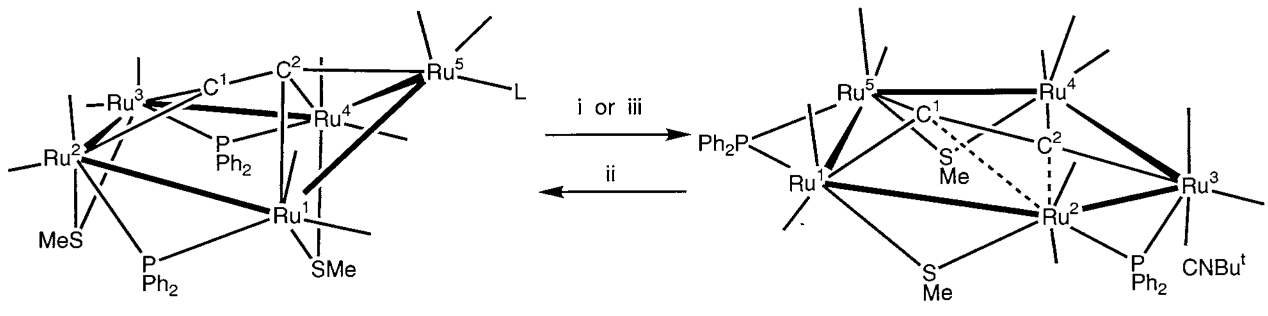
PII S0022-328X(98)00459-8



(1) L = CO
(2) L = CNBu^t

(3)

Reagents: i, L = CO: CNBu^t; ii, L = CNBu^t: − CO; iii, L = CNBu^t: + CO.

Scheme 1. Reaction of **1** with Bu^{t}NC to give two complexes, characterised as $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_n(CNBu^t)$ [$n = 10$ (**2**), 11 (**3**)].

easily isolated in a pure state. This paper describes the substitution chemistry of **1** in detail, together with the X-ray crystal structures of Bu^{t}NC and $P(OMe)_3$ complexes which confirm the site of substitution.

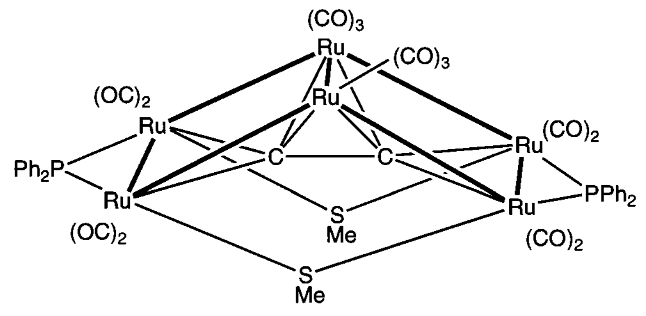
2. Results and discussion

As we have described briefly [5], **1** reacts with Bu^{t}NC to give two complexes, which were characterised as $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_n(CNBu^t)$ [$n = 10$ (**2**), 11 (**3**); Scheme 1]. While their spectroscopic properties were consistent with their solid-state structures, single-crystal X-ray structure determinations were carried out on both complexes. These showed that in the formation of green **3**, addition of Bu^{t}NC to **1** had occurred, with concomitant flattening of the Ru_5 pentagon and expansion of the average Ru–Ru separations from 2.88 Å in **1** to 2.96 Å in **3**. The reasons for these changes have been explored in detail elsewhere [8] and will not be reiterated here. On heating **3** in toluene with an N_2 purge to remove liberated CO, the colour darkened and **2** could be isolated (82%) by preparative TLC as purple crystals. The molecular structure determination showed it to be a derivative of **1** in which a CO group on the unique Ru(5) atom had been formally replaced by Bu^{t}NC. This reaction could be reversed (in 58% yield) by addition of CO. A third complex formed during the decarbonylation remains unidentified.

An alternative approach to the preparation of substituted derivatives of **1** is via the oxidative displacement of CO using trimethylamine *N*-oxide. These reactions were carried out by adding Me_3NO to solutions of the cluster carbonyls in dichloromethane containing acetonitrile until no starting material remained. For the MeCN complexes, simple evaporation and recrystallisation afforded the substitution products directly. These could be treated with the phosphorus ligand when immediate reaction occurred to give the appropriate derivatives, which were similarly isolated by evaporation and recrystallisation. In none of these reactions have we observed the formation of complexes analogous to **3**, suggesting that attack of the Me_3NO occurs directly at one of the CO groups attached to Ru(5).

The reaction between $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}$ (**1**) and acetonitrile thus gave black crystals of the lightly-stabilised cluster $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}(NCMe)$ (**4**). This complex was identified by elemental analysis and from its mass spectrum, which contained a molecular ion at m/z 1316. The IR $\nu(CO)$ spectrum was complex, containing ten medium to strong absorptions. In the ^{1}H-NMR spectrum, the presence of coordinated acetonitrile was confirmed by a signal at δ 1.95, in addition to the SMe resonances which were found at δ 0.91 and 1.25 and a broad multiplet for the Ph protons between δ 7.05 and 7.87.

Similar replacement of a CO group by acetonitrile was achieved with the larger cluster $Ru_6(\mu_6\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu_3\text{-}SMe)_2(CO)_{14}$ (**5**) [8] to give orange–red $Ru_6(\mu_6\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu_3\text{-}SMe)_2(CO)_{13}(NCMe)$ (**6**). However, this complex was not fully characterised, with the highest mass ion in the

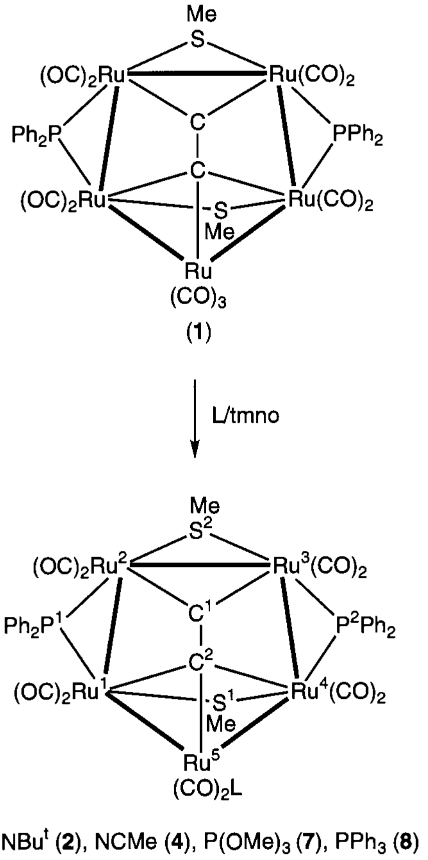


(5)

mass spectrum corresponding to $[M - MeCN]^+$ at m/z 1460. The ^{1}H-NMR spectrum of **6** contained Me resonances at δ 1.75, 1.86 and 1.99, assigned to the two SMe groups and the coordinated MeCN ligand, respectively. A satisfactory elemental analysis was not obtained.

As anticipated, ready replacement of MeCN by tertiary-phosphine or phosphite ligands occurred in these complexes. Thus the reactions of **4** with $P(OMe)_3$ and PPh_3 afforded the complexes $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}(PR_3)$ [R = OMe (**7**), Ph (**8**), respectively; Scheme 2], both being isolated in ca. 90% yield. Complex **7** was obtained as a mono-CH_2Cl_2 solvate and was characterised by elemental analysis, its mass spectrum which contained M^+ at m/z 1399, and from its ^{1}H-NMR spectrum, which contained the P–OMe doublet at δ 3.72 as well as the two SMe resonances at δ 1.01 and 1.79. The molecular structure of **7** was confirmed by a single-crystal X-ray study (below).

The analogous PPh_3 complex **8** had a similar ν(CO) spectrum with six terminal bands and the mass spectrum contained M^+ at m/z 1538. However, a satisfactory elemental analysis was not obtained. Two Ru_5 clusters could be attached to the linear acetylenic bis-*t* phosphine $C_2(PPh_2)_2$ (dppa) in a similar reaction between **4** and the ligand. Black crystals of $\{Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}\}_2(\mu\text{-dppa})$ (**9**) were obtained in 82% yield. The complex was identified from its IR ν(CO) spectrum, which was similar to that of **8**, and from its mass spectrum, which contained M^+ at m/z 2944. In the ^{1}H-NMR spectrum, the SMe protons resonated as two singlets at δ 1.04 and 1.75.



Scheme 2. Reaction of structure (**1**) with L/tmno resulting in the corresponding structures (**2**), (**4**), (**7**) and (**8**), depending on the ligand (L) used.

The substitution products could also be obtained from the direct reaction between **1** and the ligand in dichloromethane, by adding Me_3NO until no **1** remained. However, the yields obtained during these reactions were lower than those from preformed **4**. The $P(OMe)_3$ and PMe_2Ph complexes was isolated, both in 42% yield, as black crystals. Identification of the latter rests on its method of synthesis, IR ν(CO) spectrum and mass spectrum (M^+ at m/z 1413). The ^{1}H-NMR spectrum contained Me resonances at δ 1.04 and 1.78 (SMe) and a doublet at δ 2.25 (PMe_2Ph). In both of these reactions, trace amounts of other unidentified products, perhaps formed by addition or poly-substitution, were separated by TLC.

Similar reactions of the hexaruthenium cluster **6** with PPh_3 and dppa were carried out and gave black crystalline products identified as $Ru_6(\mu_6\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu_3\text{-}SMe)_2(CO)_{13}(PPh_3)$ (**10**) and $\{Ru_6(\mu_6\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu_3\text{-}SMe)_2(CO)_{14}\}_2(\mu\text{-dppa})$ (**11**), respectively. Complexes **10** and **11** had similar IR ν(CO) spectra and M^+ ions at m/z 1722 and 3314, respectively. The characteristic SMe resonances were found in the ^{1}H-NMR spectra at δ 1.59 and ca. 1.95, respectively. Mass spectral evidence for the formation of the related $P(OMe)_3$ complex [M^+ at m/z 1536, together with $[M - n\text{CO}]^+$ ($n = 1–13$)] was also obtained, but this complex was not fully characterised. We have not obtained crystals of any of these products that are suitable for an X-ray structure determination, so that the position of substitution is unknown.

2.1. *Molecular structures of $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}(L)$ [L = $CNBu^t$ (**2**) and $P(OMe)_3$ (**7**)]*

Figs. 1 and 2 contain plots of molecules of **2** and **7**, respectively, and selected bond parameters are given in Table 1, together with comparable values for **1**. The structures are very similar to that of **1** [2], one CO group on Ru(5) being replaced by the entering ligand. The relative positions of the ligands on Ru(5) in **2** and in **7** differ, the isonitrile being approximately *trans* to C(2) and in the pseudo-mirror symmetry element of the cluster, while the phosphite is found in one of the other (equivalent) positions out of that plane, being approximately *trans* to the Ru(4)–Ru(5) vector in **7**. This factor may result in the shortened Ru(5)–C(2) bond. Comparison of bond parameters in complexes **1** and **7** shows that the Ru–Ru separations are little changed in

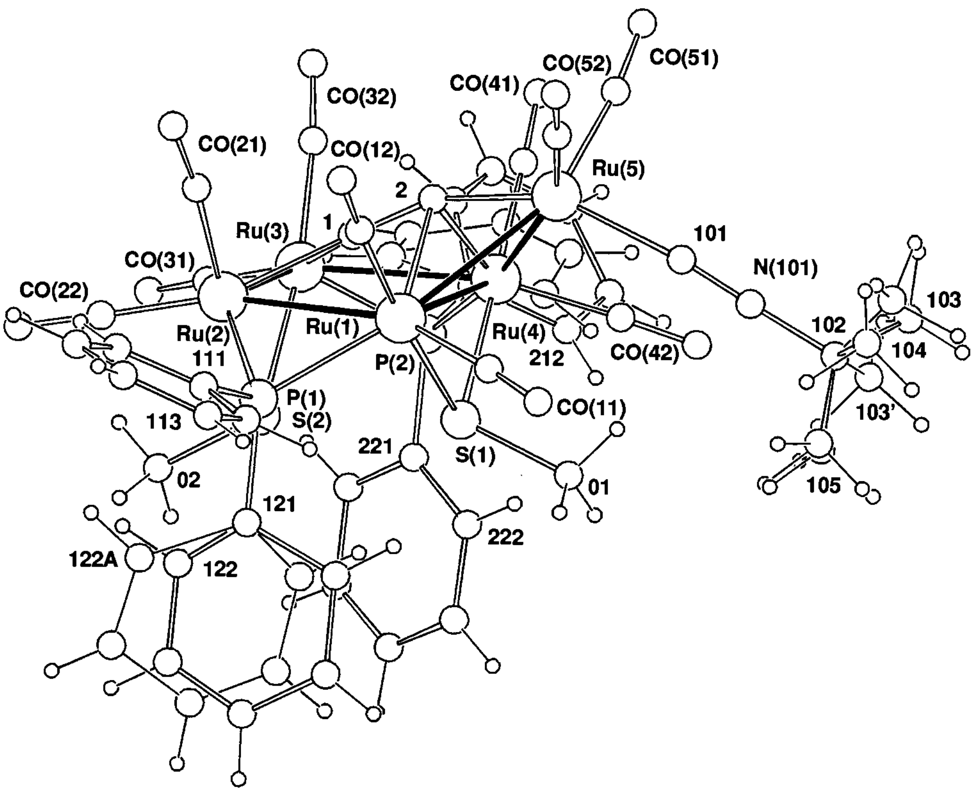


Fig. 1. Plot of a molecule of $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}(CNBu^t)$ (**2**) , showing atom numbering scheme. As a result of disordered components, non-H thermal ellipsoids have been omitted for clarity in this projection; H atoms have arbitrary radii of 0.1 Å.

7 (av. 2.887 vs. 2.885 Å in **1**), but are longer on both complexes than those found in **2**. The apparent site of substitution is on the unique Ru(5) atom. The coordination of the C_2 ligand appears to be weakened by replacement of CO by $P(OMe)_3$, average Ru–C distances being lengthened from 2.139 Å in **1** to 2.153 Å in **7**. At the same time, the C(1)–C(2) distance increases slightly, from 1.307(2) Å in **1** to 1.322(7) Å in **7**, a trend opposite to that expected if back-bonding from the cluster to the C_2 ligand was reduced in **7**. There also seems to be little correlation between the Ru(5)–C(1) distances and the C(1)–C(2) separations in the three complexes. We note that the sums of angles around C(1) are 359.9° in both complexes, so that approximate planar sp^2 coordination is achieved; however, the angles subtended at C(1) by atoms Ru(2), Ru(3) and C(2) are 82.7(5) and 83.2(2)° (Ru(2)–C(1)–Ru(3), values for **2** and **7**, respectively) and between 137.6(8) and 139.6(7)° [Ru(2 or 3)–C(1)–C(2)].

The difference in coordination about Ru(5) probably arises because of steric interaction of the OMe groups of the phosphite ligand with the μ-SMe group. However, we cannot rule out the effects of probable differences in the mechanisms of formation of these complexes. As mentioned above, the isocyanide initially adds to **1** to give **3** which then loses a CO group, while the reaction involving Me_3NO/MeCN presumably occurs by loss of CO first (by oxidation to CO_2), followed by coordination of the MeCN ligand. However, this simplistic interpretation does not explain the rearrangements observed in the μ-SMe and μ-PPh_2 groups. We have previously suggested that formation of **3** occurs by addition of Bu^tNC to Ru(1) in **1**, with concomitant migration of the SMe group from Ru(1) to Ru(4), so that the Ru(4)–Ru(5) edge becomes bridged. Concomitant rotation of the C_2 ligand and electronic reorganisation in the C_2Ru_5 core results in the C_2 ligand becoming a four-electron donor (rather than six as in **1**), preserving the CVE of **3** at 80. The formation of **2** can be envisaged to occur by loss of CO from Ru(4), followed by migration of the SMe group from Ru(4) back to Ru(3) and a 1,2-shift of the Bu^tNC from Ru(3) to Ru(4) (Scheme 1). Alternative mechanisms involving Ru–Ru bond cleavage and reformation may also be involved. The complex series of reactions required for conversion of **3** to **2** no doubt explains the relatively low yields which have been obtained.

2.2. Related chemistry

Following the above studies, we briefly examined the reactions of **1** with amines. With *n*-butylamine, a rapid reaction occurred at room temperature (r.t.) to give a dark green complex formulated as $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}(NH_2Bu)$ (**12**) by elemental analysis and observation of M^+ at m/z 1376 in the mass spectrum. The IR ν(CO) spectrum was complex and

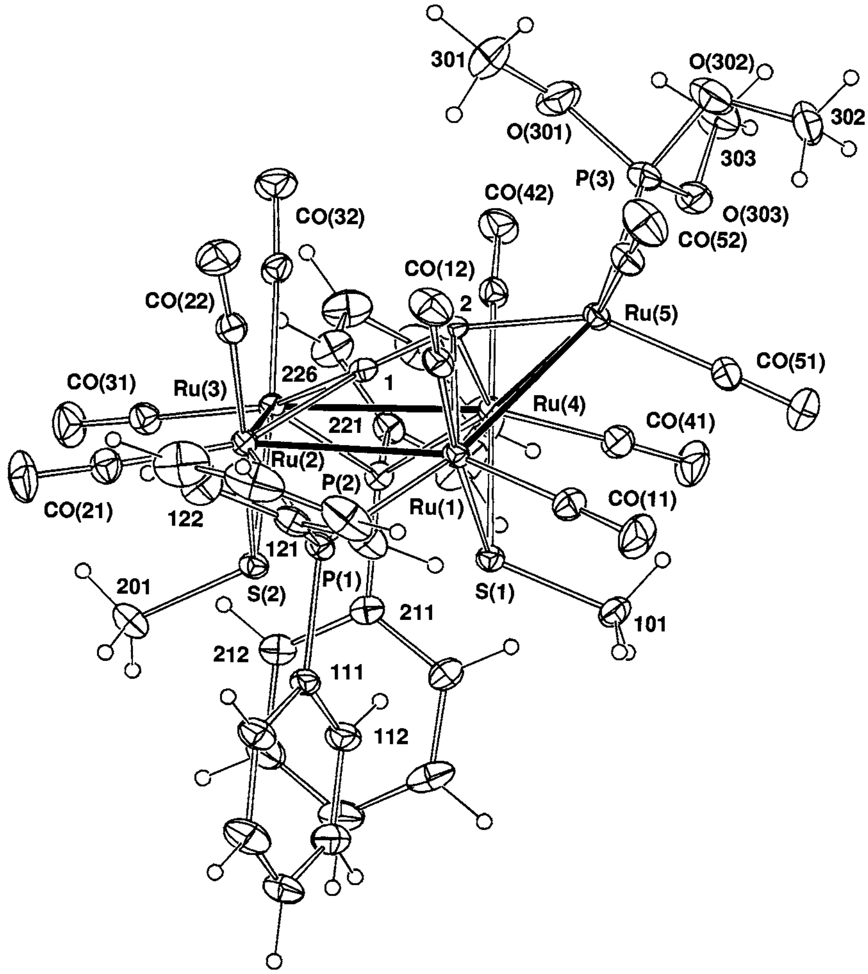
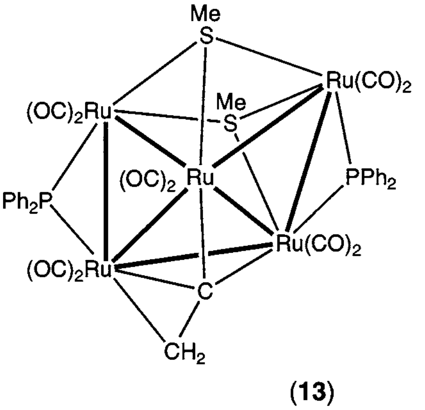


Fig. 2. Plot of a molecule of $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}\{P(OMe)_3\}$ (7), showing atom numbering scheme. Non-H atoms are shown as 20% thermal ellipsoids; H atoms have arbitrary radii of 0.1 Å.

broadly resembled those of **8** and **9**. We were not able to get a satisfactory ^1H-NMR spectrum of **12** and, although well-formed crystals were obtained, the molecular structure could not be determined.

With diethylamine and triethylamine, reactions required heating in a Carius tube for several hours. The only product which was isolated was the known vinylidene cluster, $Ru_5(\mu_5\text{-}CCH_2)(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)_2(CO)_{10}$ (**13**) [10].



(13)

This compound can be obtained from the reaction of molecular hydrogen with **1**. The source of the hydrogen in the present reactions appears to be the amine (complex **13** is not formed in the absence of the amine), although the fate of any dehydrogenation products was not determined.

3. Conclusions

Reaction of Bu^tNC with **1** proceeds by initial addition to the cluster and reorganisation of the C_2–Ru_5 interaction. In contrast, substitution of the open pentanuclear cluster $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}$ (**1**) by acetonitrile occurs at the unique Ru atom to give **4**; replacement of MeCN in **2** by $P(OMe)_3$ or PPh_3 affords the derived complexes **7** and **8**. Similar results were found for the larger cluster **5**, and in both cases, 'dumbbell' shaped bi-clusters were obtained with the linear ligand $C_2(PPh_2)_2$. These reactions provide a means of introducing further functionalised ligands into larger clusters.

Table 1
Selected bond parameters for $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}(L)$ [L = $CNBu^t$ (**2**), $P(OMe)_3$ (**7**), CO (**1**)]

	2	**7**	**1**
Bond lengths (Å)			
Ru(1)–Ru(2)	2.876(2)	2.8801(7)	2.898(1)
Ru(1)–Ru(5)	2.869(2)	2.8916(9)	2.898(1)
Ru(1)···Ru(4)	3.450(2)	3.480(1)	3.449(2)
Ru(2)–Ru(3)	2.856(2)	2.8617(9)	2.855(2)
Ru(3)–Ru(4)	2.878(2)	2.9002(8)	2.882(1)
Ru(4)–Ru(5)	2.869(2)	2.9011(9)	2.890(1)
Ru(1)–P(1)	2.326(4)	2.345(2)	—
Ru(2)–P(1)	2.284(4)	2.307(1)	2.290(1)
Ru(3)–P(2)	2.295(4)	2.300(2)	2.294(1)
Ru(4)–P(2)	2.306(4)	2.332(1)	2.341(1)
Ru(5)–P(3)	—	2.246(2)	—
Ru(1)–S(1)	2.450(3)	2.447(2)	2.454(1)
Ru(4)–S(1)	2.452(4)	2.450(1)	2.449(1)
Ru(2)–S(2)	2.397(4)	2.389(2)	2.386(1)
Ru(3)–S(2)	2.388(4)	2.391(1)	2.391(1)
Ru(2)–C(1)	2.11(1)	2.158(6)	2.133(3)
Ru(3)–C(1)	2.21(1)	2.151(5)	2.135(4)
Ru(1)–C(2)	2.22(1)	2.254(5)	2.232(3)
Ru(4)–C(2)	2.27(1)	2.247(5)	2.260(4)
Ru(5)–C(2)	1.88(1)	1.953(5)	1.936(4)
Ru(1)–C(1)	2.37(1)	2.404(5)	2.470(3)
Ru(4)–C(1)	2.41(1)	2.416(5)	2.409(4)
C(1)–C(2)	1.36(2)	1.322(7)	1.307(5)
Bond angles (°)			
Ru(2)–Ru(1)–Ru(5)	119.59(5)	120.33(2)	117.51(2)
Ru(1)–Ru(2)–Ru(3)	96.70(5)	95.97(3)	96.39(2)
Ru(2)–Ru(3)–Ru(4)	95.15(5)	96.31(3)	95.37(2)
Ru(3)–Ru(4)–Ru(5)	120.93(5)	119.63(2)	119.30(2)
Ru(4)–Ru(5)–Ru(1)	73.92(4)	73.86(2)	73.14(4)
Ru(1)–S(1)–Ru(4)	89.5(1)	90.59(5)	89.39(5)
Ru(5)–C(2)–C(1)	159.0(1)	159.5(4)	163.1(3)
C(2)–Ru(5)–L	150.5(6) [C(101)]	105.7(2)[P(3)]	114.2(2) [C0(52)]
C(2)–Ru(5)–C(51)	105.7(5)	148.0(2)	99.5(2)
C(2)–Ru(5)–C(52)	110.6(5)	112.5(2)	148.5(2) [C0(53)]
C(51)–Ru(5)–C(52)	91.5(6)	93.5(3)	94.9(2)
C(51)–Ru(5)–L	91.9(6)	91.0(2)	95.3(2)
C(52)–Ru(5)–L	91.9(6)	92.3(2)	91.9(2)

Dihedrals Ru(1)–Ru(2)–Ru(3)–Ru(4)/Ru(1)–Ru(4)–Ru(5): 44.59(4) (for **2**); 44.79(4) (for **7**); 47.79(1) (for **1**).

4. Experimental

General experimental conditions were similar to those described earlier [11]. Complexes **1** [2] and **5** [9] were prepared by the cited methods. Me_3NO was prepared by sublimation of the dihydrate (Aldrich) in vacuum. $P(OMe)_3$ (Aldrich) and PPh_3 (BDH) were used as received.

*4.1. Reaction of **1** with t-butyl isocyanide*

t-Butyl isocyanide (20 µl, 0.18 mmol) was added to a solution of **1** (50 mg, 0.038 mmol) in toluene (15 ml). After 15 min, solvent was removed and the residue separated by preparative TLC (light petroleum:acetone 10:3) into two major products. A purple band (R_f 0.5) was recrystallised from CH_2Cl_2/MeOH to yield $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}(CNBu^t)$ (**2**) (16 mg, 31%). Anal. Found: C 37.09, H 2.72, N 1.13%, *M* 1358 (MS). $C_{43}H_{35}NO_{10}P_2Ru_5S_2 \cdot 0.5CH_2Cl_2$ Calc.: C 37.33, H 2.59, N 1.00%, *M* 1358. IR (cyclohexane) ν(CO): 2043s, 2028s, 2023vs, 2015s, 2012vs, 2004m, 1998m, 1977m, 1964(sh), 1961s, 1956(sh), 1950(sh) cm^{-1}. ^1H-NMR ($CDCl_3$): δ 1.02 (3H, s, SMe), 1.59 (9H, s, CMe_3), 1.91 (3H, s, SMe), 7.07–7.81 (20H, m, Ph). FAB MS (*m*/*z*): 1358 M^+, 1329–1077 $[M - nCO]^+$ ($n = 1$–10).

A green band (R_f 0.45) was recrystallised from CH_2Cl_2/MeOH to yield $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}(CNBu^t)$ (**3**) (34 mg, 65%). Anal. Found: C 37.85, H 2.53, N 1.02%, *M* 1386 (MS). $C_{44}H_{35}NO_{11}P_2Ru_5S_2$ Calc.: C 38.15, H 2.55, N 1.01%, *M* 1386. IR (cyclohexane) ν(CO): 2064(sh), 2060vs, 2035s, 2024vs, 2012m, 2002w, 1987m, 1975m 1965vs, 1950w, 1944w cm^{-1}. ^1H-NMR ($CDCl_3$): δ 0.57 (9H, s, CMe_3), 1.39 (3H, s, SMe), 1.68 (3H, s, SMe), 7.05–8.39 (20H, m, Ph). ^{13}C-NMR ($CDCl_3$): δ 19.33, 21.65 (2 × s, SMe), 28.78 (s, C*Me*$_3$), 56.43 (s, *C*Me$_3$), 110.28 (s, C≡N), 127.12–133.49 (m, Ph), 143.65 (d, $J_{CP} = 32.2$ Hz, *ipso* C), 145.51 (d, $J_{CP} = 28.7$ Hz, *ipso* C), 146.02 (d, $J_{CP} = 15.7$ Hz, CC), 146.96 (d, $J_{CP} = 14.6$ Hz, CC), 189.97 (d, $J_{CP} = 6.9$ Hz, CO), 192.30 (d, $J_{CP} = 5.3$ Hz, CO), 193.16 (d, $J_{CP} = 4.8$ Hz, CO), 193.39 (s, CO), 199.31 (d, $J_{CP} = 3.7$ Hz, CO), 200.79 (s, CO), 202.03 (d, $J_{CP} = 6.9$ Hz, CO), 203.19 (d, $J_{CP} = 3.0$ Hz, CO), 204.68 (s, CO). FAB MS (*m*/*z*): 1386 M^+; 1358–1078 $[M - nCO]^+$ ($n = 1$–11). The green band decomposes after short periods on dry silica.

*4.2. Pyrolysis of $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}(CNBu^t)$ (**3**)*

A solution of $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}(CNBu^t)$ (**3**) (35 mg, 0.025 mmol) in toluene (15 ml) was heated at 90°C for 90 min with an N_2 purge. The solvent was removed and the residue purified by preparative TLC (light petroleum:acetone 10:3) to yield three bands. A purple band (R_f 0.6) contained recovered **3** (4 mg, 12%). The major purpleband (R_f 0.5) was recrystallised from CH_2Cl_2/MeOH to yield $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}(CNBu^t)$ (**2**) (28 mg, 82%). A trace purple band (R_f 0.4) was not identified.

*4.3. Reaction of $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}(CNBu^t)$ (**2**) with CO*

A solution of $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}$

(CNBu^t) (**2**) (35 mg, 0.026 mmol) in toluene (15 ml) was heated at 90°C for 90 min with a CO purge. The solvent was removed and the residue purlfied by preparative TLC (light petroleum:acetone 10:3) to yield three bands. The major green band (R_f 0.5) was recrystallised from CH_2Cl_2/MeOH to yield $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}(CNBu^t)$ (**3**) (21 mg, 58%). Two other minor green bands were not characterised.

4.4. Preparation of $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}(NCMe)$ (4)

A sample of Me_3NO (3–4 mg, ca. 0.047 mmol) was added to a solution of **1** (50 mg, 0.038 mmol) in CH_2Cl_2 (15 cm^3) and MeCN (1 ml) until no starting material remained. After filtration through a short column of silica the solvent was removed and the residue recrystallised from CH_2Cl_2/MeOH/MeCN to yield black crystals of $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}(NCMe)$ (**4**) (46 mg, 92%). Anal. Found: C 33.85, H 2.44, N 0.83%, *M* 1316 (MS). $C_{40}H_{29}NO_{10}P_2Ru_5S_2 \cdot 2CH_2Cl_2$ Calc.: C 33.97, H 2.24, N 0.94%, *M* 1316. IR (CH_2Cl_2) ν(CO): 2067(sh), 2062(sh), 2053(sh), 2044s, 2020vs, 2012vs, 1991m, 1981m, 1963s, 1953s cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 0.91 (3H, s, SMe), 1.25 (3H, s, SMe), 1.95 (3H, s, NCMe), 7.05–7.87 (20H, m, Ph). FAB MS (*m*/*z*): 1316 M$^+$, 1275 $[M - NCMe]^+$, 1251–999 $[M - NCMe - nCO]^+$ ($n = 1$–10).

4.5. Preparation of $Ru_6(\mu_6\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu_3\text{-}SMe)_2(CO)_{13}(NCMe)$ (6)

A sample of Me_3NO (ca. 2–3 mg, 0.03 mmol) was added to a solution of **5** (40 mg, 0.027 mmol) in CH_2Cl_2 (15 cm^3) and MeCN (1 ml) until no starting material remained. After filtration through a short column of silica the solvent was removed and the residue recrystallised from CH_2Cl_2/MeOH/MeCN to yield orange–red crystals of $Ru_6(\mu_6\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu_3\text{-}SMe)_2(CO)_{13}(NCMe)$ (**6**) (36 mg, 88%). IR (CH_2Cl_2) ν(CO): 2057s, 2029vs, 2020s, 2009m, 2003m, 1989w, 1982m, 1979(sh), 1970m, 1965m, 1954w, 1948vw, 1930vw cm$^-$ 1. ^{1}H-NMR ($CDCl_3$): δ 1.75 (3H, s, SMe), 1.86 (3H, s, SMe), 1.99 (3H, s, NCMe), 6.83–7.96 (20H, m, Ph). FAB MS (*m*/*z*): 1460 $[M - NCMe]^+$, 1432–1096 $[M - NCMe - nCO]^+$ ($n = 1$–13).

4.6. Reactions of $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}(NCMe)$ (4)

4.6.1. (a) With $P(OMe)_3$

A solution of **4** (40 mg, 0.030 mmol) and $P(OMe)_3$ (5 mg, 0.040 mmol) in CH_2Cl_2 (20 ml) was stirred at r.t. for 15 min. The solvent was removed and the residue recrystallised from CH_2Cl_2/MeOH to yield black crystals of $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}\{P(OMe)_3\}$ (**7**) (38 mg, 93%). Anal. Found: C 34.48, H 2.52%, *M* 1399 (MS). $C_{41}H_{35}O_{13}P_3Ru_5S_2 \cdot CH_2Cl_2$ Calc.: C 34.02, H 2.51%, *M* 1399. IR (CH_2Cl_2) ν(CO): 2043s, 2022s, 2013vs, 1994m, 1972m, 1957m cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.01 (3H, s, SMe), 1.79 (3H, s, SMe), 3.72 [9H, d, J_{HP} 12.8 Hz, $P(OMe)_3$], 7.00–7.32 (20H, m, Ph). FAB MS (*m*/*z*): 1399 M$^+$, 1371–1119 $[M - nCO]^+$ ($n = 1$–10).

4.6.2. (b) With PPh_3

A solution of **4** (20 mg, 0.015 mmol) and PPh_3 (5 mg, 0.019 mmol) in CH_2Cl_2 (20 ml) was stirred at r.t. for 15 min. The solvent was removed and the residue recrystallised from CH_2Cl_2/MeOH to yield black crystals of $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}(PPh_3)$ (**8**) (20 mg, 88%). Anal. Found: C 43.04, H 2.72%, *M* 1538 (MS). $C_{56}H_{41}O_{10}P_3Ru_5S_2$ Calc.: C 43.78, H 2.69%, *M* 1538. IR (CH_2Cl_2) ν(CO): 2040m, 2021s, 2010vs, 1985m, 1964m, 1955s cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.10 (3H, s, SMe), 1.76 (3H, s, SMe), 6.97–7.82 (35H, m, Ph). FAB MS (*m*/*z*): 1538 M$^+$, 1510–1258 $[M - nCO]^+$ ($n = 1$–10).

4.6.3. (c) With dppa

A solution of **4** (50 mg, 0.038 mmol) and dppa (7.5 mg, 0.019 mmol) in CH_2Cl_2 (20 ml) was stirred at r.t. for 15 min. The solvent was removed and the residue recrystallised from CH_2Cl_2/MeOH to yield black crystals of $\{Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}\}_2(\mu\text{-}dppa)$ (**9**) (46 mg, 82%). Anal. Found: C 41.53, H 2.47%, *M* 2944 (MS). $C_{102}H_{72}O_{20}P_6Ru_{10}S_4$ Calc.: C 41.64, H 2.47%, *M* 2944. IR (CH_2Cl_2) ν(CO): 2042m, 2020s, 2011vs, 1997(sh), 1991m, 1973m, 1956s cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.04 (3H, s, SMe), 1.75 (3H, s, SMe), 6.95–7.80 (60H, m, Ph).

4.7. Reactions of $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}$ (1)

4.7.1. (a) With $P(OMe)_3/Me_3NO$

A sample of Me_3NO (3–4 mg, ca. 0.047 mmol) was added to a solution of **1** (50 mg, 0.038 mmol) and $P(OMe)_3$ (6 mg, 0.048 mmol) in CH_2Cl_2 (15 cm^3) until no starting material remained. After filtration through a short column of silica the solvent was removed and the residue purified by preparative TLC (light petroleum:acetone 10:3). The major purple band (R_f 0.6) was recrystallised from CH_2Cl_2/MeOH to yield black crystals of **7** (22 mg, 42%). Three other bands were not identified.

4.7.2. (b) With PMe_2Ph/Me_3NO

A sample of Me_3NO (3–4 mg, ca. 0.047 mmol) was added to a solution of **1** (50 mg, 0.038 mmol) and

PMe_2Ph (7 mg, 0.051 mmol) in CH_2Cl_2 (15 cm^3) until no starting material remained. After filtration through a short column of silica the solvent was removed and the residue purified by preparative TLC (light petroleum:acetone 10:3). The major purple band (R_f 0.6) was recrystallised from CH_2Cl_2/MeOH to yield black crystals of $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}(PMe_2Ph)Ru_5$ (22 mg, 42%). IR (CH_2Cl_2) ν(CO): 2039m, 2018vs, 2008vs, 1985m, 1965m, 1954m; (cyclohexane) 2041s, 2021vs, 2009vs, 1996m, 1989m, 1970m, 1960(sh), 1957m, 1950(sh), 1934w cm^{-1}. ^1H-NMR ($CDCl_3$): δ 1.04 (3H, s, SMe), 1.78 (3H, s, SMe), 2.25 (6H, d, J_{HP} 9.4 Hz, PMe_2), 6.97–7.88 (25H, m, Ph). FAB MS (*m*/*z*): 1413 M^+, 1385–1133, $[M-nCO]^+$ ($n=1-10$). Three other complexes analogous to those obtained in the reaction with $P(OMe)_3$ were not identified.

4.7.3. (c) With NH_2Bu

A solution of **1** (50 mg, 0.038 mmol) and *n*-butylamine (10 mg, 0.14 mmol) in CH_2Cl_2 (10 cm^3) was stirred at r.t. for 15 min. The solvent was removed and the residue recrystallised from CH_2Cl_2/MeOH to yield dark green crystals of $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}(NH_2Bu)$ (**12**) (41 mg, 79%). Anal. Found: C 37.35, H 2.83, N 1.06%, *M* 1376 (MS). $C_{43}H_{37}NO_{11}P_2Ru_5S_2$ Calc.: C 37.56, H 2.71, N 1.02%, *M* 1376. IR (cyclohexane) ν(CO): 2069m, 2061s, 2029vs, 2013m, 2002m, 1996m, 1990m, 1974m, 1966s, 1954m, 1945w, 1927vw(br) cm^{-1}. FAB MS (*m*/*z*): 1376 M^+, 1348–1068 $[M-nCO]^+$ ($n=1-11$). A light brown band (R_f 0.45, 5 mg) was not identified.

4.7.4. (d) With $NHEt_2$

A solution of **1** (50 mg, 0.038 mmol) and diethylamine (100 mg, 1.4 mmol) in toluene (10 cm^3) was heated to 95°C in a Carius tube for 9 h. The solvent was removed and the residue purified by preparative TLC (light petroleum:acetone 10:3) to yield three bands. The major brown band (R_f 0.4) was recrystallised from CH_2Cl_2/MeOH to yield black crystals of $Ru_5(\mu_5\text{-}CCH_2)(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)_2(CO)_{10}$ (**13**) (45 mg, 93%), identified by comparison with an authentic sample.

4.7.5. (e) With NEt_3

A solution of **1** (50 mg, 0.038 mmol) and triethylamine (100 mg, 1.1 mmol) in toluene (10 cm^3) was heated to 120°C in a Carius tube for 40 h. The solvent was removed and the residue purified by preparative TLC (light petroleum:acetone 10:3) to yield one major band. The major brown band (R_f 0.4) was recrystallised from CH_2Cl_2/MeOH to yield black crystals of **13** (31 mg, 64%).

4.8. Reactions of $Ru_6(\mu_6\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu_3\text{-}SMe)_2(CO)_{13}(NCMe)$ (**6**)

4.8.1. (a) With PPh_3

A solution of **6** (20 mg, 0.014 mmol) and PPh_3 (4 mg, 0.015 mmol) in CH_2Cl_2 (20 ml) was stirred at r.t. for 15 min. The solvent was removed and the residue recrystallised from CH_2Cl_2/MeOH to yield black crystals of $Ru_6(\mu_6\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu_3\text{-}SMe)_2(CO)_{13}(PPh_3)$ (**10**) (22 mg, 92%). Anal. Found: C 41.28, H 2.61%, *M* 1722 (MS). $C_{59}H_{41}O_{13}P_3Ru_6S_2$ Calc.: C 41.17, H 2.40%, *M* 1722. IR (CH_2Cl_2) ν(CO): 2056s, 2031vs, 2019s, 2009(sh), 2003m, 1979m, 1965m, 1951(sh); (cyclohexane) 2057s, 2035vs, 2030(sh), 2021s, 2013m, 2004m, 1999(sh), 1992m, 1983m, 1971m, 1965m, 1953m cm^{-1}. ^1H-NMR ($CDCl_3$): 1.59 (3H, s, SMe), 2.00 (3H, s, SMe), 6.78–7.83 (35H, m, Ph). FAB MS (*m*/*z*): 1722 M^+, 1694–1442 $[M-nCO]^+$ ($n=1-10$).

4.8.2. (b) With $P(OMe)_3$

Similarly, a solution of **6** (25 mg, 0.017 mmol) and $P(OMe)_3$ (3 mg, 0.024 mmol) in CH_2Cl_2 (20 ml) at r.t. for 15 min gave black crystals, tentatively identified as $Ru_6(\mu_6\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu_3\text{-}SMe)_2(CO)_{13}\{P(OMe)_3\}$ (24 mg, 89%). FAB MS (*m*/*z*): 1536 M^+, 1508–1172 $[M-nCO]^+$ ($n=1-13$).

4.8.3. (c) With dppa

A solution of **6** (75 mg, 0.051 mmol) and dppa (10 mg, 0.026 mmol) in CH_2Cl_2 (20 ml) was stirred at r.t. for 15 min. The solvent was removed and the residue recrystallised from CH_2Cl_2/MeOH to yield black crystals of $\{Ru_6(\mu_6\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu_3\text{-}SMe)_2(CO)_{14}\}_2(\mu\text{-}dppa)$ (**11**) (73 mg, 86%). Anal. Found: C 39.25, H 2.21%, *M* 3314 (MS). $C_{108}H_{72}O_{26}P_6Ru_{12}S_4$ Calc.: C 39.16, H 2.19%, *M* 3314. IR (CH_2Cl_2) ν(CO): 2057s, 2033vs, 2020s, 2010(sh), 2004m, 1980m, 1966m, 1951(sh); (cyclohexane) 2058s, 2036vs, 2022s, 2013m, 2005m, 1992w, 1983m, 1971m, 1957w, 1953w cm^{-1}. ^1H-NMR ($CDCl_3$): δ 1.59 (6H, s, SMe), 1.95 (6H, s, SMe), 6.78–7.75 (60H, m, Ph).

4.9. Crystallography

Unique data sets were measured at ca. 295 K within the limit $2\theta_{max}=50°$ using a Syntex P2 diffractometer ($2\theta/\theta$ scan mode, monochromatic Mo–K_α radiation, λ 0.71073 Å); *N* independent reflections were obtained, N_o with $I>3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after Gaussian absorption correction. Anisotropic thermal parameters were refined for the non-H atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals *R*, R_w on $|F|$ are given, statisti-

Table 2
Non-hydrogen positional and isotropic displacement parameters for (**2**)

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.76516(4)	0.43251(5)	0.9721(1)	0.0571(4)
Ru(2)	0.78391(5)	0.51433(5)	0.7526(1)	0.0655(5)
Ru(3)	0.67105(5)	0.60443(5)	0.7716(1)	0.0677(5)
Ru(4)	0.62821(4)	0.54021(5)	0.9931(1)	0.0554(4)
Ru(5)	0.65853(4)	0.40883(5)	0.9969(1)	0.0598(5)
C(11)	0.7821(6)	0.3783(7)	1.128(2)	0.092(7)
O(11)	0.7945(5)	0.3460(5)	1.221(1)	0.120(6)
C(12)	0.7966(5)	0.3657(6)	0.854(1)	0.073(6)
O(12)	0.8163(4)	0.3219(4)	0.793(1)	0.100(5)
C(21)	0.7974(5)	0.4516(6)	0.624(1)	0.069(6)
O(21)	0.8088(4)	0.4167(5)	0.5422(9)	0.104(5)
C(22)	0.8244(7)	0.5503(7)	0.644(2)	0.105(9)
O(22)	0.8502(7)	0.5762(7)	0.567(1)	0.19(1)
C(31)	0.6724(8)	0.6739(8)	0.677(1)	0.11(1)
O(31)	0.6716(7)	0.7204(6)	0.619(1)	0.18(1)
C(32)	0.6209(6)	0.5952(6)	0.649(1)	0.085(7)
O(32)	0.5923(5)	0.5923(5)	0.565(1)	0.118(6)
C(41)	0.5642(5)	0.5460(6)	0.891(1)	0.073(6)
O(41)	0.5259(4)	0.5512(5)	0.829(1)	0.097(5)
C(42)	0.5867(5)	0.5356(6)	1.160(1)	0.072(6)
O(42)	0.5613(4)	0.5353(5)	1.2645(9)	0.098(5)
C(51)	0.5872(5)	0.4104(6)	0.940(1)	0.070(6)
O(51)	0.5474(4)	0.4105(5)	0.893(1)	0.103(5)
C(52)	0.6933(6)	0.3250(6)	0.954(1)	0.083(7)
O(52)	0.7128(4)	0.2757(5)	0.921(1)	0.126(6)
S(1)	0.7157(1)	0.5200(2)	1.1190(3)	0.062(1)
C(01)	0.7056(6)	0.4926(7)	1.294(1)	0.084(7)
S(2)	0.7515(2)	0.6015(2)	0.8975(4)	0.074(2)
C(02)	0.7811(8)	0.6599(8)	0.838(2)	0.12(1)
C(1)	0.7043(5)	0.5038(5)	0.815(1)	0.059(5)
C(2)	0.6831(4)	0.4593(5)	0.866(1)	0.053(5)
P(1)	0.8464(1)	0.4595(2)	0.9149(4)	0.067(2)
C(111)	0.9114(5)	0.3980(6)	0.863(1)	0.075(6)
C(112)	0.9361(7)	0.3529(8)	0.954(2)	0.13(1)
C(113)	0.9876(8)	0.3042(9)	0.924(3)	0.18(1)
C(114)	1.0129(7)	0.3030(9)	0.798(3)	0.17(1)
C(115)	0.9899(8)	0.349(1)	0.705(2)	0.18(1)
C(116)	0.9386(6)	0.3968(8)	0.736(2)	0.113(9)
C(121)	0.8734(6)	0.5000(7)	1.029(1)	0.094(7)
C(122)[a]	0.900(1)	0.533(1)	0.998(3)	0.10(2)
C(123)[a]	0.921(1)	0.566(1)	1.088(3)	0.09(1)
C(124)[a]	0.915(1)	0.554(2)	1.222(4)	0.17(3)
C(125)[a]	0.893(2)	0.506(2)	1.274(3)	0.16(3)
C(126)[a]	0.866(1)	0.480(2)	1.181(3)	0.10(2)
C(122A)[a]	0.920(2)	0.526(2)	0.956(4)	0.14(2)
C(123A)[a]	0.946(2)	0.559(2)	1.016(6)	0.21(3)
C(124A)[a]	0.913(2)	0.585(2)	1.149(5)	0.17(3)
C(125A)[a]	0.870(2)	0.569(2)	1.204(4)	0.15(2)
C(126A)[a]	0.850(1)	0.528(1)	1.134(4)	0.12(2)
P(2)	0.6093(2)	0.6446(2)	0.9579(4)	0.073(2)
C(211)	0.5331(6)	0.6941(6)	0.936(1)	0.103(8)
C(212)[a]	0.4962(9)	0.707(1)	1.074(2)	0.07(1)
C(213)[a]	0.439(1)	0.738(1)	1.068(2)	0.06(1)
C(214)[a]	0.414(1)	0.753(1)	0.932(4)	0.10(2)
C(215)[a]	0.449(1)	0.736(1)	0.817(3)	0.10(2)
C(216)[a]	0.503(1)	0.702(1)	0.823(3)	0.08(1)
C(212A)[a]	0.497(1)	0.701(1)	1.014(2)	0.12(1)
C(213A)[a]	0.4362(7)	0.747(1)	0.982(2)	0.11(1)
C(214A)[a]	0.4307(6)	0.781(1)	0.877(3)	0.16(2)
C(215A)[a]	0.480(1)	0.783(1)	0.796(3)	0.24(3)
C(216A)[a]	0.529(1)	0.738(2)	0.813(3)	0.16(2)
C(221)	0.6330(5)	0.6897(6)	1.070(1)	0.076(6)
C(222)	0.6492(7)	0.6696(7)	1.201(2)	0.098(8)
C(223)	0.6706(8)	0.7022(8)	1.285(2)	0.14(1)
C(224)	0.6746(7)	0.7560(9)	1.238(2)	0.14(1)
C(225)	0.6602(8)	0.7760(8)	1.113(2)	0.14(1)
C(226)	0.6376(8)	0.7443(8)	1.025(2)	0.12(1)
C(101)	0.6394(5)	0.3868(6)	1.196(2)	0.083(7)
N(101)	0.6295(5)	0.3794(5)	1.314(1)	0.092(6)
C(102)	0.6160(7)	0.3705(8)	1.457(1)	0.116(9)
C(103)[a]	0.552(1)	0.389(2)	1.484(4)	0.19(3)
C(104)[a]	0.645(2)	0.301(2)	1.494(4)	0.16(2)
C(105)[a]	0.629(3)	0.415(2)	1.534(4)	0.21(4)
C(103′)[a]	0.568(2)	0.426(3)	1.499(4)	0.23(3)
C(104′)[a]	0.600(2)	0.322(2)	1.465(4)	0.21(3)
C(105′)[a]	0.662(2)	0.367(2)	1.537(3)	0.15(3)
Cl(1)[a]	1.0054(6)	0.4651(7)	1.415(1)	0.20(1)
Cl(2)[a]	1.0463(5)	0.3601(6)	1.249(1)	0.186(8)
Cl(3)[a]	0.9326(6)	0.3985(7)	1.365(1)	0.184(9)
C(0)[a]	0.988(1)	0.423(2)	1.295(3)	0.12(2)

[a] Site occupancy factor = 0.5.

cal weights derivative of $\sigma^2(I) = \sigma^2(I_{\mathrm{diff}}) + 0.0004\sigma^4(I_{\mathrm{diff}})$ being used. Computation used the XTAL 2.6 program system [12] implemented by S.R. Hall; neutral atom complex scattering factors were employed. Pertinent results are given in Figs. 1 and 2 and Tables 1–3. The material deposited with the Cambridge Crystallographic Data Centre comprises structure factor amplitudes, thermal and H atom parameters and full non-H geometries.

4.10. *Crystal and refinement data*

4.10.1. *$Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}(CNBu^t)\cdot 0.5CHCl_3$ (**2**)*

Molecular formula $C_{43}H_{35}NO_{10}P_2Ru_5S_2\cdot 0.5CHCl_3$, $M = 1416.9$. Triclinic, space group $I\bar{1}$, $a = 24.777(12)$, b = 23.153(9), c = 9.658(4) Å, $\alpha = 86.50(3)$, $\beta = 85.85(3)$, $\gamma = 69.84(3)°$, $V = 5184$ Å^3, $Z = 4$, $D_{\mathrm{calc.}} = 1.815$ g cm^{-3}, $F(000) = 2764$. Crystal dimensions: $0.33 \times 0.08 \times 0.23$ mm, $\mu(\text{Mo–K}_\alpha) = 17.0$ cm^{-1}, A^* (min, max) = 1.14, 1.59. $N = 8622$, $N_o = 5128$, $R = 0.061$, $R_w = 0.060$.

4.10.2. *$Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}\{P(OMe)_3\}\cdot CHCl_3$ (**7**)*

Molecular formula $C_{41}H_{35}O_{13}P_3Ru_5S_2\cdot CHCl_3$, $M = 1517.5$. Triclinic, space group $P\bar{1}$, $a = 20.283(5)$, $b = 14.013(4)$, $c = 9.746(3)$ Å, $\alpha = 81.84(2)$, $\beta = 87.44(2)$, $\gamma = 75.96(2)°$, $V = 2660$ Å^3, $Z = 2$, $D_{\mathrm{calc.}} = 1.89$ g cm^{-3}, $F(000) = 1480$. Crystal dimensions: $0.08 \times 0.18 \times 0.39$ mm, $\mu(\text{Mo–K}_\alpha) = 16.0$ cm^{-1}, A^* (min, max) = 1.12, 1.37. $N = 8931$, $N_o = 6957$, $R = 0.031$, $R_w = 0.034$.

Table 3
Non-hydrogen positional and isotropic displacement parameters for (**7**)

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.22562(2)	0.82737(3)	0.69414(4)	0.0303(2)
Ru(2)	0.33322(2)	0.68482(3)	0.84667(4)	0.0301(2)
Ru(3)	0.28197(2)	0.51483(3)	0.82282(4)	0.0300(1)
Ru(4)	0.16218(2)	0.62156(3)	0.66545(4)	0.0301(1)
Ru(5)	0.08621(2)	0.81247(3)	0.73522(4)	0.0339(2)
C(11)	0.1874(3)	0.9390(4)	0.5700(6)	0.048(2)
O(11)	0.1657(3)	1.0092(3)	0.4935(5)	0.076(2)
C(12)	0.2126(3)	0.9080(4)	0.8382(6)	0.041(2)
O(12)	0.2032(2)	0.9584(3)	0.9210(5)	0.067(2)
C(21)	0.4210(3)	0.6383(4)	0.9212(6)	0.048(2)
O(21)	0.4732(2)	0.6136(4)	0.9707(5)	0.083(2)
C(22)	0.3074(3)	0.7459(4)	1.0073(6)	0.043(2)
O(22)	0.2941(2)	0.7776(4)	1.1087(5)	0.074(2)
C(31)	0.3500(3)	0.4004(4)	0.8839(6)	0.043(2)
O(31)	0.3902(2)	0.3312(3)	0.9213(5)	0.072(2)
C(32)	0.2246(3)	0.4809(4)	0.9708(6)	0.043(2)
O(32)	0.1925(2)	0.4622(4)	1.0649(5)	0.070(2)
C(41)	0.0971(3)	0.6398(4)	0.5269(6)	0.050(2)
O(41)	0.0598(2)	0.6463(4)	0.4408(5)	0.081(2)
C(42)	0.1091(3)	0.5488(4)	0.7818(6)	0.039(2)
O(42)	0.0761(2)	0.5019(3)	0.8430(5)	0.061(2)
C(51)	0.0329(3)	0.8626(4)	0.5735(6)	0.047(2)
O(51)	0.0019(3)	0.8887(4)	0.4747(5)	0.077(2)
C(52)	0.0617(3)	0.9346(5)	0.8078(6)	0.050(2)
O(52)	0.0468(2)	1.0067(3)	0.8537(6)	0.081(2)
S(1)	0.22911(7)	0.71945(9)	0.5161(1)	0.0342(5)
C(101)	0.1799(3)	0.7892(4)	0.3669(5)	0.046(2)
S(2)	0.35930(7)	0.5812(1)	0.6673(1)	0.0345(5)
C(201)	0.4458(3)	0.5047(4)	0.6836(7)	0.052(2)
C(1)	0.2311(3)	0.6680(4)	0.8286(5)	0.030(2)
C(2)	0.1686(3)	0.7245(4)	0.8188(5)	0.032(2)
P(1)	0.34164(7)	0.8246(1)	0.6970(1)	0.0345(5)
C(111)	0.3997(3)	0.8180(4)	0.5472(5)	0.040(2)
C(112)	0.3899(3)	0.7686(4)	0.4383(6)	0.049(2)
C(113)	0.4340(3)	0.7617(5)	0.3262(6)	0.062(3)
C(114)	0.4868(3)	0.8070(5)	0.3188(7)	0.065(3)
C(115)	0.4967(4)	0.8571(5)	0.4233(8)	0.075(3)
C(116)	0.4541(3)	0.8626(4)	0.5374(7)	0.054(3)
C(121)	0.3620(3)	0.9250(4)	0.7749(6)	0.044(2)
C(122)	0.4026(4)	0.9063(5)	0.8895(7)	0.065(3)
C(123)	0.4170(5)	0.9831(7)	0.9493(9)	0.090(4)
C(124)	0.3903(5)	1.0780(7)	0.893(1)	0.092(5)
C(125)	0.3495(4)	1.1002(5)	0.778(1)	0.083(4)
C(126)	0.3350(3)	1.0232(5)	0.7189(8)	0.066(3)
P(2)	0.23502(7)	0.4682(1)	0.6400(1)	0.0334(5)
C(211)	0.2892(3)	0.4498(4)	0.4869(5)	0.038(2)
C(212)	0.3500(3)	0.3780(4)	0.4956(6)	0.052(2)
C(213)	0.3934(3)	0.3688(5)	0.3832(8)	0.067(3)
C(214)	0.3776(4)	0.4297(6)	0.2603(7)	0.067(3)
C(215)	0.3178(4)	0.5004(5)	0.2512(6)	0.064(3)
C(216)	0.2725(3)	0.5111(4)	0.3622(6)	0.046(2)
C(221)	0.1981(3)	0.3607(4)	0.6605(6)	0.040(2)
C(222)	0.1653(5)	0.3405(6)	0.5527(8)	0.091(4)
C(223)	0.1314(5)	0.2659(7)	0.567(1)	0.113(5)
C(224)	0.1311(4)	0.2088(5)	0.6909(9)	0.077(4)
C(225)	0.1638(4)	0.2247(5)	0.8003(8)	0.074(3)
C(226)	0.1969(4)	0.3019(4)	0.7857(6)	0.058(3)
P(3)	−0.00061(8)	0.7595(1)	0.8454(2)	0.0475(6)
O(301)	0.0159(3)	0.6883(4)	0.9893(5)	0.079(2)
C(301)	0.0468(5)	0.7106(7)	1.1003(8)	0.101(4)
O(302)	−0.0613(2)	0.8392(4)	0.9028(5)	0.083(2)
C(302)	−0.1004(4)	0.9197(6)	0.8128(9)	0.097(4)
O(303)	−0.0318(2)	0.6928(3)	0.7623(4)	0.058(2)
C(303)	−0.0823(4)	0.6410(6)	0.8217(8)	0.081(4)
Cl(11)[a]	0.3870(6)	1.113(1)	0.289(1)	0.342(9)
Cl(12)[a]	0.2997(3)	1.0132(4)	0.2489(7)	0.215(4)
Cl(13)[a]	0.2725(6)	1.219(1)	0.205(2)	0.43(1)
Cl(21)[b]	0.2666(6)	1.1879(8)	0.391(1)	0.114(5)
Cl(22)[b]	0.2650(6)	1.201(2)	0.143(2)	0.24(1)
Cl(23)[b]	0.4048(5)	1.127(1)	0.251(1)	0.092(4)
C(0)	0.307(1)	1.114(2)	0.290(3)	0.28(1)

[a] Site occupancy factor = 0.75. [b] Site occupancy factor = 1−0.75.

4.11. Abnormal features/variations in procedure

(a) Complex **2**: Rings C(12n, 21n) were modelled with carbon atoms $n > 1$ disordered over two sets of sites, occupancies set at 0.5 after trial refinement; disorder was modelled similarly in the t-butyl and chloroform moieties. The structure was refined in space group $I\bar{1}$; the true space group, however, is primitive, the additional reflections being very weak and limited in scope, and incapable of supporting a meaningful refinement. It is not clear which components of the disorder, if any, would be eliminated in a lower symmetry space group. Derivative geometries should be used with appropriate circumspection.

(b) Complex **7**: The chloroform solvent was modelled in terms of a pair of disordered components, site occupancies set at x, $1 - x$, with $x = 0.75$, after trial refinement.

Acknowledgements

We thank the Australian Research Council for financial support and Johnson Matthey Technology Centre for a generous loan of $RuCl_3 \cdot nH_2O$.

References

[1] M.I. Bruce, Coord. Chem. Rev. 166 (1997) 91.
[2] C.J. Adams, M.I. Bruce, B.W. Skelton, A.H. White, J. Chem. Soc. Dalton Trans. (1997) 2937.
[3] C.J. Adams, M.I. Bruce, E. Horn, B.W. Skelton, E.R.T. Tiekink, A.H. White, J. Chem. Soc. Dalton Trans. (1993) 3299.
[4] M.I. Bruce, J. Cluster Sci. 8 (1997) 293.
[5] C.J. Adams, M.I. Bruce, B.W. Skelton, A.H. White, Chem. Commun. (1996) 975.
[6] G.A. Foulds, B.F.G. Johnson, J. Lewis, J. Organomet. Chem. 296 (1985) 147.
[7] H.G. Ang, W.L. Kwik, W.K. Leong, J. Organomet. Chem. 379 (1989) 325.
[8] G. Frapper, J.-F. Halet, M.I. Bruce, Organometallics 16 (1997) 2590.

[9] C.J. Adams, M.I. Bruce, B.W. Skelton, A.H. White, J. Chem. Soc. Chem. Commun. (1993) 446.

[10] C.J. Adams, M.I. Bruce, M. Schulz, B.W. Skelton, A.H. White, J. Organomet. Chem. 472 (1994) 285.

[11] C.J. Adams, M.I. Bruce, B.W. Skelton, A.H. White, J. Organomet. Chem. 452 (1993) 121.

[12] S.R. Hall, J.M. Stewart (Eds.), XTAL Users' Manual, Version 2.6, Universities of Western Australia and Maryland, 1989.