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Alkyne-based derivatives of $[Ru_6C(CO)_{17}]$ and the stepwise synthesis of $[Ru_6C(CO)_{13}(\eta^5\text{-}C_5H_3Ph_2)(\mu_3\text{-}CPh)]$

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A systematic synthetic route to the hexanuclear cluster compound $[Ru_6C(CO)_{13}(\eta^5\text{-}C_5H_3Ph_2)(\mu_3\text{-}CPh)]$ has been elaborated in which a number of stable intermediates have been isolated and characterised. The reaction of $[Ru_6C(CO)_{17}]$ with Me_3NO and phenylacetylene afforded the alkyne derivative $[Ru_6C(CO)_{15}(PhC_2H)]$ **1**. Further treatment of **1** with Me_3NO and an excess of phenylacetylene resulted in the formation of two isomers $[Ru_6C(CO)_{14}\{C(Ph)CHC(Ph)CH\}]$ **2** and $[Ru_6C(CO)_{14}\{C(Ph)CHCHC(Ph)\}]$ **3**. Both contain five-membered metallocyclic rings formed by the head-to-head coupling of phenylacetylene in one isomer and the head-to-tail coupling in the other. Reaction of isomer **2** with Me_3NO and phenylacetylene leads to $[Ru_6C(CO)_{13}(\eta^5\text{-}C_5H_3Ph_2)(\mu_3\text{-}CPh)]$ **4**. The molecular structure of one of the isomers, **3**, has been established by single-crystal X-ray crystallography.

Arene derivatives of $[Ru_6C(CO)_{17}]$, *e.g.* $[Ru_6C(CO)_{14}(\eta^6\text{-arene})]$, have been well documented[1–4] and can be synthesized, for example, by the thermolysis of $[Ru_3(CO)_{12}]$ in the presence of an arene.[1] We have been interested to see whether or not these arene derivatives may also be obtained from the trimerisation of alkynes, a process which has been observed with mononuclear complexes[5] and more recently in the reaction of $[Ru_3(CO)_9(MeCN)_3]$ with disubstituted alkynes.[6] The reaction of $[Ru_6C(CO)_{17}]$ with dimethylacetylene leads to the formation of $[Ru_6C(CO)_{15}(MeC_2Me)]$, $[Ru_6C(CO)_{13}(MeC_2Me)_2]$, $[Ru_6C(CO)_{12}(MeC_2Me)_3]$ and $[Ru_6C(CO)_{10}(MeC_2Me)_4]$ where the direct substitution of carbonyl ligands by dimethylacetylene occurs with no apparent evidence of oligomerisation.[7] We have found however that the reaction of $[Ru_6C(CO)_{17}]$ with phenylacetylene proceeds *via* a different pathway and recently reported the structure of $[Ru_6C(CO)_{13}(\eta^5\text{-}C_5H_3Ph_2)(\mu_3\text{-}CPh)]$ in which C≡C bond scission and oligomerisation occur to form both an η^5-bound diphenylcyclopentadienyl ligand and a μ_3-bound CPh alkylidyne ligand (see Fig. 1).[8] In this paper we report the detailed results of this reaction, including the isolation and characterisation of two isomers, $[Ru_6C(CO)_{14}\{C(Ph)CHC(Ph)CH\}]$ and $[Ru_6C(CO)_{14}\{C(Ph)CHCHC(Ph)\}]$, the first of which is the precursor to $[Ru_6C(CO)_{13}(\eta^5\text{-}C_5H_3Ph_2)(\mu_3\text{-}CPh)]$.

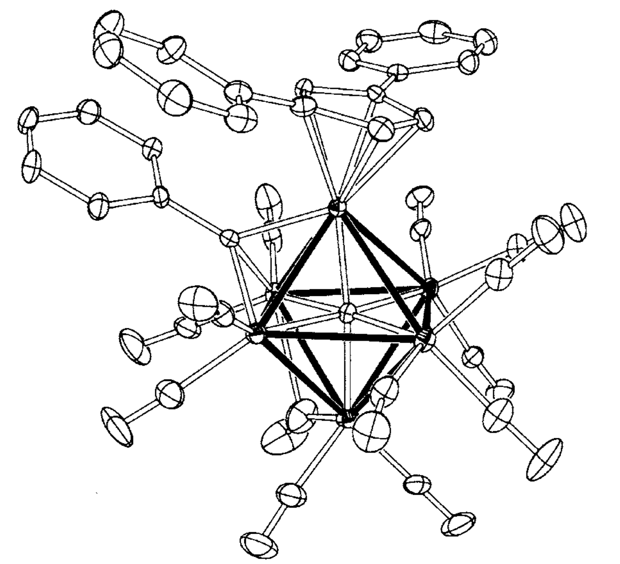

Fig. 1 Molecular structure of $[Ru_6C(CO)_{13}(\eta^5\text{-}C_5H_3Ph_2)(\mu_3\text{-}CPh)]$

Results and Discussion

The reaction of $[Ru_6C(CO)_{17}]$ with phenylacetylene is shown in Scheme 1 and spectroscopic data for all compounds reported are given in Table 1. In all reactions Me_3NO is employed as an oxidative-decarbonylation reagent. Treatment of $[Ru_6C(CO)_{17}]$ with 2 molar equivalents of Me_3NO in the presence of an excess of phenylacetylene results primarily in the formation of $[Ru_6C(CO)_{15}(PhC_2H)]$ **1** in 25% yield. This is a known compound, previously synthesized from the oxidation of $[Ru_6C(CO)_{16}]^{2-}$ with $[Fe(\eta\text{-}C_5H_5)_2]^+$ in the presence of phenylacetylene.[9] In it the phenylacetylene behaves as a four-electron donor, exhibiting an μ_3-η^2 bonding mode, one of the most common modes observed on a triangular face of metal atoms.[10,11] Three minor products, $[Ru_6C(CO)_{14}\{C(Ph)CHC(Ph)CH\}]$ **2**, $[Ru_6C(CO)_{14}\{C(Ph)CHCHC(Ph)\}]$ **3** and $[Ru_6C(CO)_{13}(\eta^5\text{-}C_5H_3Ph_2)(\mu_3\text{-}CPh)]$ **4** are also formed during this reaction, although in very low yield. Further treatment of **1** with 2 equivalents of Me_3NO and phenylacetylene leads to the formation of **2**–**4** in greater yield. The spectroscopic data for compounds **2** and **3** are consistent with the formation of two isomers in which a second acetylene has been incorporated into the system to form five-membered metallacyclopentadiene rings. The FAB mass spectra reveal the same molecular ion peak and the solution IR spectra in CH_2Cl_2 are very similar showing evidence of both terminal and bridging [$\nu(CO) \approx 1850\ cm^{-1}$] carbonyl ligands. The ^1H NMR spectrum of **2** consists of resonances due to the phenyl rings and also doublets at δ 10.09 and 6.69 corresponding to H^2 and H^1 respectively. The spectrum of **3** consists of a singlet at δ 5.43 corresponding to H^1. The metallocyclic ring is formed from the head-to-tail coupling of phenylacetylene in the case of compound **2** and the head-to-head coupling of phenylacetylene in **3**.

Unfortunately, crystals of compound **2** suitable for X-ray analysis could not be obtained, although a structure of the analogous *tert*-butylacetylene compound has been determined[12] and we expect that of **2** to be similar. The molecular

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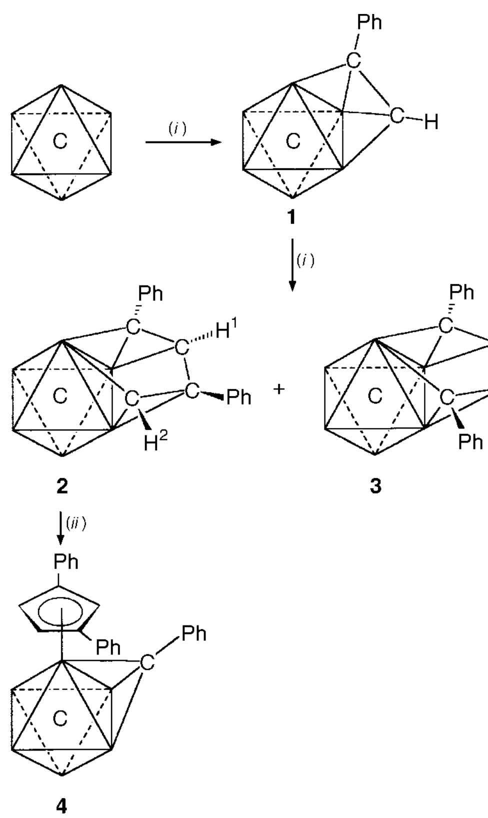
Table 1 Spectroscopic data

	Compound	IR [a], $\tilde{\nu}(CO)/cm^{-1}$	^1H NMR [b], δ	FAB mass spectrum, m/z [c]
1	$[Ru_6C(CO)_{15}(PhC_2H)]$	2089m, 2045vs, 2038s (sh), 2022m, 2015m, 1989w	10.18 (s, 1 H), 7.49–7.37 (m, 5 H)	1140 (1140)
2	$[Ru_6C(CO)_{14}\{C(Ph)CHC(Ph)CH\}]$	2080m, 2045s, 2033vs, 1984w, 1960w, 1850w (br)	10.09 (d, 1 H), 7.86–7.10 (m, 10 H), 6.69 (d, 1 H) [d]	1215 (1214)
3	$[Ru_6C(CO)_{14}\{C(Ph)CHCHC(Ph)\}]$	2079m, 2044s, 2033vs, 1983w (sh), 1848w	7.40–7.16 (m, 10 H), 5.43 (s, 2 H)	1214 (1214)
4	$[Ru_6C(CO)_{13}(\eta^5\text{-}C_5H_3Ph_2)(\mu_3\text{-}CPh)]$	2073m, 2031s, 2019m, 2000w, 1981w (sh), 1959 (w)	7.77–7.49 (m, 5 H), 7.32–7.11 (m, 10 H), 5.64 (t, 1 H), 5.45 (d, 2 H)	1286 (1288)

[a] In CH_2Cl_2. [b] In CD_2Cl_2 unless otherwise stated. [c] Calculated values in parentheses. [d] In $(CD_3)_2CO$.

Table 2 Bond lengths (Å) for compound **3**

Ru(1)–Ru(2)	2.772(1)	Ru(4)–C(1)	2.03(1)
Ru(1)–Ru(3)	2.782(1)	Ru(5)–C(1)	2.04(1)
Ru(1)–Ru(4)	2.779(1)	Ru(6)–C(1)	1.992(9)
Ru(1)–Ru(5)	3.017(1)	Ru(1)–C(12)	2.120(9)
Ru(2)–Ru(3)	2.802(1)	Ru(1)–C(15)	2.064(9)
Ru(2)–Ru(5)	2.894(1)	Ru(2)–C(12)	2.126(9)
Ru(2)–Ru(6)	2.968(1)	Ru(2)–C(13)	2.251(8)
Ru(3)–Ru(4)	2.947(1)	Ru(3)–C(14)	2.217(8)
Ru(3)–Ru(6)	2.911(1)	Ru(3)–C(15)	2.204(9)
Ru(4)–Ru(5)	2.886(1)	C(12)–C(13)	1.430(13)
Ru(4)–Ru(6)	2.965(1)	C(12)–C(121)	1.483(13)
Ru(5)–Ru(6)	2.848(1)	C(13)–C(14)	1.463(12)
Ru(1)–C(1)	2.084(9)	C(14)–C(15)	1.435(13)
Ru(2)–C(1)	2.03(1)	C(15)–C(151)	1.472(12)
Ru(3)–C(1)	2.06(1)		



Scheme 1 Synthesis of alkyne-based derivatives of $[Ru_6C(CO)_{17}]$: (*i*) 2 equivalents Me_3NO, PhC_2H; (*ii*) Me_3NO, PhC_2H

structure of **3** has been established (Fig. 2) and selected bond lengths are given in Table 2. It consists of an octahedron of ruthenium atoms with an interstitial carbido atom. There are fourteen carbonyl groups, of which thirteen are terminal and one is bridging. The CO ligands are essentially linear and the bridging CO is slightly asymmetric [Ru(1)–C(41) 2.058(10), Ru(4)–C(41) 2.107(9) Å]. The Ru–Ru bond lengths lie in the range 2.772(1)–3.017(1) Å, with the three shortest associated with Ru(1). The structure contains a ruthenacyclopentadiene ring which lies across one of the triangular faces [Ru(1)–Ru(2)–Ru(3)] of the octahedron. This ring is formed by the head-to-head linking of two phenylacetylene ligands and incorporates the Ru(1) atom. There are two σ bonds to Ru(1) [Ru(1)–C(12), Ru(1)–C(15)] and two π bonds C(12)–C(13) bound to Ru(2) and C(14)–C(15) to Ru(3). The ruthenacyclopentadiene moiety is not bound symmetrically to the triangular face, the two σ bonds Ru(1)–C(12) and Ru(1)–C(15) having values of 2.120(9) and 2.064(9) Å respectively. One of the π interactions is also asymmetric [Ru(2)–C(12) 2.126(9), Ru(2)–C(13) 2.251(8) Å]. These features have also been observed in the trinuclear osmium cluster $[Os_3(CO)_9\{C(SiMe_3)C(Me)CHC(Ph)\}]$.[13] The dihedral angle of the metallocyclic ring [between the C(12)–Ru(1)–C(15) and C(12)–C(13)–C(14)–C(15) planes] is 31.4° and the C–C bond lengths within the ring lie in the range 1.43(1)–1.46(1) Å. Again these values are very similar to those found in $[Os_3(CO)_9\{C(SiMe_3)C(Me)CHC(Ph)\}]$ and also in $[Mo_2Co_2(CO)_2(C_5H_4Me)_2S_3(PhCCH)_2]$ and $[\{Ru(C_5Me_5)(\mu\text{-}H)\}_3\{\mu_3\text{-}\eta^4\text{-}C(Me)CHCHCH\}]$.[14,15] In this system the organo-ligand behaves as a six-electron donor giving an electron count of 86, characteristic of these octahedral carbido-clusters.

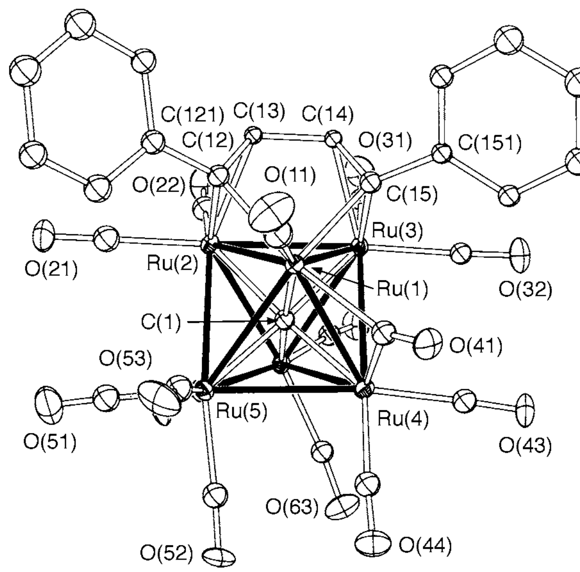


Fig. 2 Molecular structure of $[Ru_6C(CO)_{14}\{C(Ph)CHCHC(Ph)\}]$ **3** with the hydrogen atoms omitted for clarity. The C atoms of the carbonyl groups bear the same numbering as that of the corresponding O atoms

To summarise, the addition of phenylacetylene to $[Ru_6C(CO)_{17}]$ initially leads to a monosubstituted compound where the alkyne is bound in a μ_3-η^2 mode, which is then followed by the formation of a metallacyclopentadiene ring. This system has also been observed in the synthesis of $[Mo_2Co_2(CO)_2(C_5H_4Me)_2S_3(PhCCH)_2]$.[14] Further reaction of phenylacetylene and Me_3NO with compound **3** leads solely to the recovery of starting material. The analogous reaction with isomer **2** however results in the formation of **4**. Sequential addition of phenylacetylene to $[Ru_6C(CO)_{17}]$ therefore leads ultimately to oligomerisation to a substituted η^5-cyclopentadiene ring *via* two intermediates.

These reactions involving $[Ru_6C(CO)_{17}]$ and phenylacetylene are unusual in several respects. First is the formation of the five-membered metallacyclopentadiene ring as observed in compounds **2** and **3**. This in itself is not uncommon in alkyne cluster chemistry, particularly in the reactions of certain trinuclear clusters. However, the formation of a metallacyclic ring facially bound on a triangular face is unusual, with only four other examples structurally characterised to date.[13–16] Another interesting feature is the isolation and characterisation of two isomers on insertion of the second alkyne, whereas in previous examples only one isomer has been observed. These two compounds also represent the first examples of such a ring forming on a hexanuclear cluster compound. Finally, and as reported before, an important aspect of this work is the formation of $[Ru_6C(CO)_{13}(\eta^5\text{-}C_5H_3Ph_2)(\mu_3\text{-CPh})]$ **4** in which C≡C bond scission and oligomerisation occur to form both an η^5-bound diphenylcyclopentadienyl ligand and a μ_3-bound CPh alkylidyne ligand.[8] Such formation of substituted η^5-cyclopentadiene rings has been reported elsewhere,[17–19] for example $[Pt_2Ru_6(\mu_6\text{-C})(CO)_{16}(\mu\text{-}\eta^5\text{-}C_5Et_4)(\mu_3\text{-}EtC_2Et)]$ exhibits a metallated tetraethylcyclopentadienyl ligand derived from the coupling of two molecules of diethylacetylene with the fifth member of the ring derived from a carbido atom of a fragmented cluster.[19] The number of examples where the alkyne oligomerises to give an organic cyclic ligand however remains very small.

Experimental

Reactions were routinely carried out using standard Schlenk-line techniques under an atmosphere of nitrogen, with dry, dioxygen-free solvents. Products were separated using thin-layer chromatography (TLC) on plates supplied by Merck coated with a 0.25 mm layer of Kieselgel 60 F_{254}. Phenylacetylene (Aldrich) was used without further purification. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrometer in CH_2Cl_2 using NaCl cells, positive-ion fast atom bombardment mass spectra using a Kratos MS50TC spectrometer, with CsI as calibrant, and ^{1}H NMR spectra on a Bruker AM-250 spectrometer, referenced to internal $SiMe_4$.

Syntheses

$[Ru_6C(CO)_{15}(PhC_2H)]$ 1. An excess of phenylacetylene (0.5 cm^3) was added to a solution of $[Ru_6C(CO)_{17}]$ (150 mg, 0.14 mmol) in CH_2Cl_2 (70 cm^3) and the mixture cooled to −78 °C. A solution of Me_3NO (23 mg, 0.3 mmol) in CH_2Cl_2 (5 cm^3) was added and the mixture allowed to warm to room temperature over 30 min. After filtering through silica, the solvent was removed under reduced pressure. The products were separated by TLC using CH_2Cl_2–hexane (3 : 7) as eluent which yielded one major brown band of $[Ru_6C(CO)_{15}(PhC_2H)]$ **1** (40 mg, 0.035 mmol); a red band of $[Ru_6C(CO)_{14}\{C(Ph)CHC(Ph)CH\}]$ **2** (≈3 mg) and a third band which, on further separation (TLC) using CH_2Cl_2–hexane–ethyl acetate (1 : 8 : 1) as eluent, revealed $[Ru_6C(CO)_{14}\{C(Ph)CHCHC(Ph)\}]$ **3** (≈3 mg) and $[Ru_6C(CO)_{13}(\eta^5\text{-}C_5H_3Ph_2)(\mu_3\text{-CPh})]$ **4** (≈2 mg).

$[Ru_6C(CO)_{14}\{C(Ph)CHC(Ph)CH\}]$ 2 and $[Ru_6C(CO)_{14}\{C(Ph)CHCHC(Ph)\}]$ 3. An excess of phenylacetylene (0.5 cm^3) was added to a solution of $[Ru_6C(CO)_{15}(PhC_2H)]$ **1** (150 mg, 0.13 mmol) in CH_2Cl_2 (70 cm^3) and the mixture cooled to −78 °C. A solution of Me_3NO (23 mg, 0.3 mmol) in CH_2Cl_2 (5 cm^3) was added and the mixture allowed to warm to room temperature over 30 min. After filtering through silica, the solvent was removed under reduced pressure. Separation by TLC using CH_2Cl_2–hexane (3 : 7) as eluent yielded two bands. The first red band consisted of $[Ru_6C(CO)_{14}\{C(Ph)CHC(Ph)CH\}]$ **2** (30 mg, 0.025 mmol). Further purification of the second band using CH_2Cl_2–hexane–ethyl acetate (1 : 8 : 1) as eluent revealed a red band of $[Ru_6C(CO)_{14}\{C(Ph)CHCHC(Ph)\}]$ **3** (12 mg, 0.01 mmol) and a green band of $[Ru_6C(CO)_{13}(\eta^5\text{-}C_5H_3Ph_2)(\mu_3\text{-CPh})]$ **4** (10 mg, 0.008 mmol).

$[Ru_6C(CO)_{13}(\eta^5\text{-}C_5H_3Ph_2)(\mu_3\text{-CPh})]$ 4. An excess of phenylacetylene (0.5 cm^3) was added to a solution of $[Ru_6C(CO)_{14}\{C(Ph)CHC(Ph)CH\}]$ **2** (30 mg, 0.025 mmol) in CH_2Cl_2 (70 cm^3) and the mixture cooled to −78 °C. A solution of Me_3NO (2 mg, 0.027 mmol) in CH_2Cl_2 (5 cm^3) was added and the mixture allowed to warm to room temperature over 30 min. After filtering through silica, the solvent was removed under reduced pressure. The products were separated by TLC using CH_2Cl_2–hexane as eluent which yielded two bands, a red band of $[Ru_6C(CO)_{14}\{C(Ph)CHCHC(Ph)\}]$ and a green band of $[Ru_6C(CO)_{13}(\eta^5\text{-}C_5H_3Ph_2)(\mu_3CPh)]$ **4** (5 mg, 0.004 mmol).

Crystallography

Crystals of $[Ru_6C(CO)_{14}\{C(Ph)CHCHC(Ph)\}]$ **3** suitable for X-ray analysis were grown from a CH_2Cl_2–hexane solution of the compound at −20 °C.

Crystal data. $C_{31}H_{12}O_{14}Ru_6{\cdot}CH_2Cl_2$, $M = 1299.75$, monoclinic, space group $P2_1/n$, $a = 13.653(2)$, $b = 14.996(3)$, $c = 18.775(3)$ Å, $\beta = 108.939(12)°$, $U = 3635.9(11)$ Å^3 (by least-squares refinement of 2θ values for 56 reflections measured at ±ω, $\lambda = 0.710\ 73$ Å), $Z = 4$, $D_c = 2.374$ g cm^{-3}, $F(000) = 2464$. Dark red lath, dimensions 0.51 × 0.19 × 0.17 mm, μ(Mo-Kα) = 2.643 mm^{-1}.

Data were measured on a Stoë-Stadi-4 diffractometer using graphite-monochromated Mo-Kα radiation and a ω–θ scan mode at 150.0(2) K. A total of 4773 independent reflections were measured ($2.61 \leqslant \theta \leqslant 22.58°$, $-14 \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 16$, $0 \leqslant l \leqslant 20$) of which 3333 were observed $[F_o \geqslant 4\sigma(F_o)]$. The data were corrected for Lorentz-polarisation effects and an empirical absorption correction based on azimuthal scan data was applied (minimum, maximum transmission coefficients 0.482, 0.556).

The structure was solved by direct methods and Fourier-difference syntheses. Refinement (on F^2) was by full-matrix least squares with isotropic thermal parameters for the carbon atoms and anisotropic displacement parameters for all other non-hydrogen atoms. The hydrogen atoms were placed in calculated positions and refined riding on their respective carbon atoms. A weighting scheme $\{\Sigma w(F_o^2 - F_c^2)^2$, $w = 1/[\sigma^2(F_o^2) + (0.0349P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ and σ was obtained from counting statistics} gave a satisfactory agreement analysis. At convergence, $R1 = 0.0399$ (observed data) and $wR2 = 0.0829$ (all data) for 327 parameters, $S = 0.999$, minimum, maximum residual electron density peaks −0.647, 1.124 e Å^{-3}.

All crystallographic calculations were performed using the SHELXTL-PC package[20] and SHELXL 93 program.[21]

Acknowledgements

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References

1 B. F. G. Johnson, R. D. Johnston and J. Lewis, *J. Chem. Soc. A*, 1968, 2865.
2 P. J. Dyson, B. F. G. Johnson, J. Lewis, M. Martinelli, D. Braga and F. Grepioni, *J. Am. Chem. Soc.*, 1993, **115**, 9062.

3 D. Braga, F. Grepioni, E. Parisini, P. J. Dyson, A. J. Blake and B. F. G. Johnson, *J. Chem. Soc., Dalton Trans.*, 1993, 2951.
4 D. Braga, F. Grepioni, B. F. G. Johnson, H. Chen and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1991, 2559.
5 K. Jonas, E. Deffense and D. Habermann, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 716.
6 A. J. Edwards, N. E. Leadbetter, J. Lewis and P. Raithby, *J. Chem. Soc., Dalton Trans.*, 1995, 3785.
7 B. F. G. Johnson, P. J. Dyson, A. J. Blake and R. Mallors, *Organometallics*, in the press.
8 J. L. Haggitt, B. F. G. Johnson, A. J. Blake and S. Parsons, *J. Chem. Soc., Chem. Commun.*, 1995, 1263.
9 S. R. Drake, B. F. G. Johnson, J. Lewis, G. Conole and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1990, 995.
10 E. Sappa, A. Tiripicchio and P. Braunstein, *Chem. Rev.*, 1983, **83**, 203.
11 P. R. Raithby and M. J. Rosales, *Adv. Inorg. Chem. Radiochem.*, 1985, **29**, 169.
12 J. L. Haggitt and B. F. G. Johnson, unpublished work.
13 A. A. Koridze, N. M. Astakhova, F. M. Dolgushin, A. I. Yanovsky, Y. Y. Struchkov and P. V. Petrovskii, *Organometallics*, 1995, **14**, 2167.
14 U. Riaz, M. D. Curtis, A. Rheingold and B. S. Haggerty, *Organometallics*, 1990, **9**, 2647.
15 H. Suzuki, Y. Takaya, T. Takemori and M. Tanaka, *J. Am. Chem. Soc.*, 1994, **116**, 10 779.
16 Y. Chi, H.-Y. Hsu, S.-M. Peng and G.-H. Lee, *J. Chem. Soc., Chem. Commun.*, 1991, 1023.
17 S. Aime, L. Milone, E. Sappa and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, 1977, 227.
18 E. Sappa, A. Tiripicchio and A. M. Manotti Lanfredi, *J. Chem. Soc., Dalton Trans.*, 1978, 552.
19 R. D. Adams and W. Wu, *J. Cluster Sci.*, 1993, **4**, 245.
20 G. M. Sheldrick, SHELXTL-PC, release 4.4, Siemens Analytical X-Ray Instruments, Madison, WI, 1992.
21 G. M. Sheldrick, SHELXL 93, Program for structure refinement, University of Göttingen, 1993.

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