

Synthesis of Homo- and Hetero-bimetallic Complexes incorporating the $[(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_9\text{H}_6)]$ Ligand

Gary M. Diamond,^a Malcolm L. H. Green,^a Neil A. Popham^a and Alexander N. Chernega^b

^a Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR

^b Chemical Crystallography Laboratory, 9 Parks Road, Oxford, UK OX1 3PD

The new bimetallic complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{MCl}_2\{(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_9\text{H}_6)\}\text{M}^*\text{Cl}_2(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Zr}$, $\text{M}^* = \text{Zr}$, Hf ; $\text{M} = \text{Hf}$, $\text{M}^* = \text{Zr}$, Hf), $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2\{(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_9\text{H}_6)\}\text{ZrCl}_2(\eta^5\text{-C}_5\text{Me}_5)]$, $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2\{(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_9\text{H}_6)\}\text{Rh}(\text{CO})_2]$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2\{(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_9\text{H}_6)\}\text{Mn}(\text{CO})_3]$ have been prepared from the precursors $[(\text{Me}_2\text{C}(\eta^5\text{-C}_5\text{H}_4)(\eta^2\text{-C}_9\text{H}_6))\text{M}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}]$ ($\text{M} = \text{Zr}$ **1**, Hf **2**); the X-ray crystal structure of **1** is reported.

Bimetallic complexes in which two reactive transition-metal centres are held in close proximity may show cooperative behaviour and may exhibit new types of reactivity not shown by otherwise analogous mononuclear species.¹⁻⁵ In our search for new Ziegler-Natta and Fischer-Tropsch catalysts we have prepared a series of new, chiral homo- and hetero-bimetallic complexes involving both early and late transition metals. In these bimetallic compounds the two metals are bridged by the $[(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_9\text{H}_6)]$ ligand.

We have recently reported the synthesis of the *ansa*-bridged compound $\{[\text{Me}_2\text{C}(\eta^5\text{-C}_5\text{H}_4)(\eta^2\text{-C}_9\text{H}_6)]\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}\}$ **1**.⁶ Here we show that **1** reacts readily with early and late transition metal compounds to give homo- and hetero-bimetallic complexes. We also now report the X-ray crystal structure of **1**.[†] The molecular structure is shown in Fig. 1 and, as previously proposed,⁶ compound **1** adopts a bent-metallocene type structure with the indenyl group bonded in an η^2 fashion to the metal. This $\text{M}-\eta^2$ -indenyl fragment readily reacts with transition metal halides.

In a typical reaction, a mixture of **1** (0.50 g, 1.21 mmol) and $[(\eta^5\text{-C}_5\text{H}_5)\text{HfCl}_3\cdot\text{DME}]$ (0.53 g, 1.21 mmol) in toluene was heated to 110°C with stirring for 15 h. Reduction of volume and cooling to -20°C afforded yellow crystals of $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2\{(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_9\text{H}_6)\}\text{HfCl}_2(\eta^5\text{-C}_5\text{H}_5)]$ **3** from toluene. Similarly, **1** reacts with $[(\eta^5\text{-C}_5\text{Me}_5)\text{-ZrCl}_3\cdot 2\text{THF}]$ to give yellow crystals of $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2\{(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_9\text{H}_6)\}\text{ZrCl}_2(\eta^5\text{-C}_5\text{Me}_5)]$ **7**.

A similar reaction between the hafnium analogue of **1**, namely $[(\text{Me}_2\text{C}(\eta^5\text{-C}_5\text{H}_4)(\eta^2\text{-C}_9\text{H}_6))\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}]$ **2**, with $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_3\cdot\text{DME}]$ yields yellow crystals of $[(\eta^5\text{-C}_5\text{H}_5)\text{HfCl}_2\{(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_9\text{H}_6)\}\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_5)]$ **4**.

The homobimetallic complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2\{(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_9\text{H}_6)\}\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_5)]$ **5** and $[(\eta^5\text{-C}_5\text{H}_5)\text{-HfCl}_2\{(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_9\text{H}_6)\}\text{HfCl}_2(\eta^5\text{-C}_5\text{H}_5)]$ **6** may also be synthesised by reaction between **1** and $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_3\cdot\text{DME}]$ or **2** and $[(\eta^5\text{-C}_5\text{H}_5)\text{HfCl}_3\cdot\text{DME}]$ respectively, but are more conveniently prepared by the reaction between the dilithium salt $[\text{Li}_2(\text{C}_5\text{H}_4)\text{CMe}_2(\text{C}_9\text{H}_6)]$ and 2 equiv. of $[(\eta^5\text{-C}_5\text{H}_5)\text{MCl}_3\cdot\text{DME}]$ ($\text{M} = \text{Zr}$, Hf).

Treatment of **1** (0.285 g, 0.69 mmol) in diethyl ether with a solution of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (0.135 g, 0.35 mmol), also in diethyl ether, at room temp. for 30 min gives dark-orange crystals of $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2\{(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_9\text{H}_6)\}\text{Rh}(\text{CO})_2]$ **8** from diethyl ether. Similarly, treatment of **1** (0.5 g, 1.21 mmol) with $[\text{Mn}(\text{CO})_5\text{Cl}]$ (0.28 g, 1.21 mmol) in THF at 70°C for 5 h gives yellow-orange crystals of $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2\{(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_9\text{H}_6)\}\text{Mn}(\text{CO})_3]$ **9** from a mixture of toluene

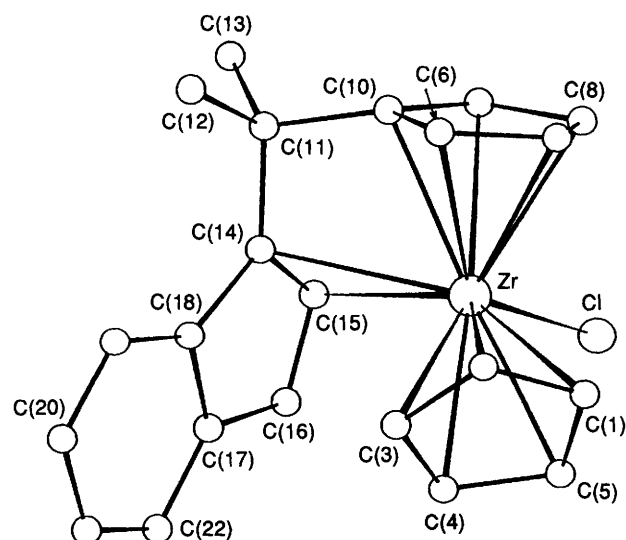
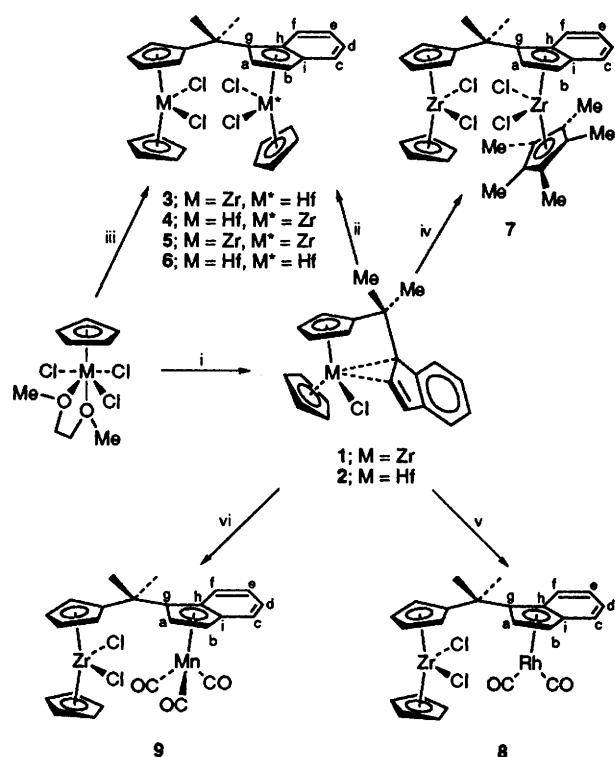


Fig. 1 Molecular structure of **1**. Selected interatomic distances (Å) and angles (°): Zr-Cl 2.489(2), Zr-C(14) 2.587(8), Zr-C(15) 2.497(8), Zr-C(16) 3.141(9), Zr-C(18) 3.329(7), Zr-C(C₅H₅)_{mean} 2.51, Zr-C(C₅H₄)_{mean} 2.47, Zr-Cp 2.212, Zr-Cp' 2.165, C(14)-C(15) 1.43(1), C(15)-C(16) 1.40(1), C(11)-C(14)-C(18) 131.8(8), C(10)-C(11)-C(14) 101.5(6), Zr-C(14)-C(15) 70.2(4), Cl-Zr-C(14) 117.1(2), Cp-Zr-Cp' 129.1. Cp and Cp' denote centroids of (C₅H₅) and (C₅H₄) rings respectively. The Zr, Cl, C(14) and C(15) atoms are approximately co-planar (deviations from best least-squares plane less than 0.11 Å).



Scheme 1 Reagents and conditions: i, $[\text{Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_9\text{H}_6)]\text{Li}_2\cdot 0.6\text{Et}_2\text{O}$, toluene, room temp., 16 h, 65–70% yield; ii, $[(\eta^5\text{-C}_5\text{H}_5)\text{M}^*\text{Cl}_3\cdot\text{DME}]$, toluene **3** or THF **4**, reflux, 16 h, 75–80% yield; iii, 0.5 equiv. $[\text{Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_9\text{H}_6)]\text{Li}_2\cdot 0.6\text{Et}_2\text{O}$, toluene, reflux, 19 h, 70–80% yield; iv, $[(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}_3\cdot 2\text{THF}]$, toluene, reflux, 16 h, 77% yield; v, $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, diethyl ether, room temp., 30 min, 60% yield; vi $[\text{Mn}(\text{CO})_5\text{Cl}]$, THF, reflux, 5 h, 66% yield

and light petroleum. These reactions are summarised in Scheme 1.

The new compounds 3–9 have been characterised by elemental analysis, ^1H and ^{13}C NMR spectroscopy \ddagger and, where appropriate, by IR spectroscopy. \S We propose η^5 (rather than η^3) coordination of the indenyl ligand to rhodium in compound 8 on the basis of the ^{13}C chemical shifts of the ring-junction carbon atoms. These lie between δ 117.6 and 113.3, *ca.* 18 to 13 ppm upfield compared with indenyl sodium. Baker and Tulip 7 have correlated the hapticity of indenyl ligands with this chemical shift difference, and comparison with their results suggests that compound 8 shows η^5 coordination of the indenyl ligand, similar to that observed in $[(\text{C}_9\text{H}_7)\text{Rh}(\text{CO})_2]$. 8

In conclusion, we have shown that compounds 1 and 2 are versatile reagents for the selective synthesis of both hetero- and homo-bimetallic complexes with unsymmetrical ligand environments. This is the first example of the formation of bimetallic complexes of this type *via* a metathesis reaction between two transition-metal centres.

We thank Imperial Chemical Industries plc for a CASE award (to G. M. D.) and the SERC for a Quota award (to N. A. P.).

Received, 7th September 1993; Com. 3/05354G

Footnotes

\dagger Crystal data: Compound 1; $\text{C}_{22}\text{H}_{21}\text{ClZr}$, $M = 412.08$, tetrahedral, space group $P4_21c$, $a = b = 22.794(1)$, $c = 7.0667(8)$ Å, $V = 3671.8$ Å 3 , $F(000) = 1680$, $Z = 8$, $D_c = 1.49$ g cm $^{-3}$, $\mu = 7.35$ cm $^{-1}$, crystal size *ca.* 0.22 \times 0.28 \times 0.45 mm, 4174 total (3696 independent) reflections, $R = 0.044$ and $R_w = 0.050$ from 1552 reflections with $I > 3\sigma(I)$ (217 variables, observations/variables 7.15), maximum peak in final Fourier difference synthesis 0.57 e Å $^{-3}$.

Data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-K α radiation ($\omega/2\theta$ scan mode, ratio of scan rates $\omega/\theta = 1.2$, $\theta_{\text{max}} = 32.5^\circ$). The structure was solved by direct methods and refined by full-matrix least-squares technique in the anisotropic approximation (Chebyshev weighting scheme, parameters 9.65, -6.15, 7.84, -0.81). 9 About 75% of hydrogen atoms were located in the difference Fourier maps, positions of the remainder were calculated geometrically. In the final refinement, all hydrogen atoms were included with the fixed positional and thermal parameters. Corrections for Lorentz and polarisation effects and empirical correction for absorption 10 were applied. Anomalous dispersion contributions were included in the calculated structure factors. Crystallographic calculations were carried out using the CRYSTALS program package 11 on a Micro VAX 3800 computer. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

\ddagger Selected NMR data (J/Hz , δ/ppm): Compound 3; δ_{H} (300 MHz, CD_2Cl_2 , room temp.) 7.57 [1 H, d, $J(\text{H}_f\text{H}_e)$ 9, H_f], 7.53 [1 H, d, $J(\text{H}_c\text{H}_d)$ 8, H_c], 7.18 (1 H, m, H_e), 7.13 (1 H, m, H_d), 6.74 [1 H, d, $J(\text{H}_a\text{H}_b)$ 4, H_a], 6.71 [1 H, pseudo q, $J(\text{HH})$ 3, C_5H_4], 6.51 [1 H, d, $J(\text{H}_b\text{H}_a)$ 4, H_b], 6.43 [5 H, s, $\text{Zr}(\text{C}_5\text{H}_5)$], 6.40 [1 H, pseudo q, $J(\text{HH})$ 3, C_5H_4], 6.15 (2 H, m, C_5H_4), 6.01 [5 H, s, $\text{Hf}(\text{C}_5\text{H}_5)$], 2.10 (3 H, s, Me), 2.01 (3 H, s, Me); δ_{C} (75.5 MHz, CD_2Cl_2) 142.1 [s, $\text{C}_{\text{ipso}}(\text{C}_5\text{H}_4)$], 127.7 (s, $\text{C}_{\text{g, h or i}}$), 126.2 [d, $J(\text{CH})$ 166, C_e], 126.0 (s, $\text{C}_{\text{g, h or i}}$), 125.8 [d, $J(\text{CH})$ 163, C_e], 125.1 [d, $J(\text{CH})$ 164, C_f], 124.7 [d, $J(\text{CH})$ 166, C_d], 122.6 (s, $\text{C}_{\text{g, h or i}}$), 122.2 [d, $J(\text{CH})$ 173, C_a], 118.4 [d, $J(\text{CH})$ 179, C_5H_4], 116.7 [d, $J(\text{CH})$ 176, C_5H_4], 116.4 [d, $J(\text{CH})$ 173, $\text{Zr}(\text{C}_5\text{H}_5)$], 115.3 [d, $J(\text{CH})$ 174, $\text{Hf}(\text{C}_5\text{H}_5)$], 113.7 [d, $J(\text{CH})$ 175, C_5H_4], 111.5 [d, $J(\text{CH})$ 173, C_5H_4], 99.6 [d, $J(\text{CH})$ 177, C_b], 39.2 (s, CMe_2), 29.1 (s, Me), 28.1 (s, Me).

4; δ_{H} (300 MHz, CD_2Cl_2) 7.57 (1 H, d, H_f), 7.52 (1 H, d, H_e), 7.19 (1 H, m, H_e), 7.14 (1 H, m, H_d), 6.74 (1 H, d, H_a), 6.66 (1 H, d, H_b), 6.63 (1 H, pseudo q, C_5H_4), 6.33 [5 H, s, $\text{Hf}(\text{C}_5\text{H}_5)$], 6.29 (1 H, pseudo q, C_5H_4), 6.12 [5 H, s, $\text{Zr}(\text{C}_5\text{H}_5)$], 6.04 (2 H, m, C_5H_4), 2.09 (3 H, s, Me), 2.00 (3 H, s, Me).

5; δ_{H} (300 MHz, CD_2Cl_2) 7.56 (1 H, d, H_f), 7.53 (1 H, d, H_e), 7.19 (1 H, m, H_e), 7.14 (1 H, m, H_d), 6.75 (1 H, d, H_a), 6.73 (1 H, pseudo q, C_5H_4), 6.67 (1 H, d, H_b), 6.43 (5 H, s, C_5H_5), 6.40 (1 H, pseudo q, C_5H_4), 6.14 (2 H, m, C_5H_4), 6.13 (5 H, s, C_5H_5), 2.09 (3 H, s, Me), 2.00 (3 H, s, Me).

6; δ_{H} (300 MHz, CD_2Cl_2) 7.58 (1 H, d, H_f), 7.53 (1 H, d, H_e), 7.18 (1 H, m, H_e), 7.13 (1 H, m, H_d), 6.74 (1 H, d, H_a), 6.61 (1 H, pseudo q, C_5H_4), 6.50 (1 H, d, H_b), 6.33 (5 H, s, C_5H_5), 6.29 (1 H, pseudo q, C_5H_4), 6.06 (2 H, m, C_5H_4), 6.00 (5 H, s, C_5H_5), 2.08 (3 H, s, Me), 2.00 (3 H, s, Me).

7; δ_{H} (300 MHz, CD_2Cl_2) 7.51 (1 H, d, H_f), 7.43 (1 H, d, H_e), 7.14 (1 H, m, H_e), 7.08 (1 H, m, H_d), 6.73 (1 H, pseudo q, C_5H_4), 6.38 (5 H, s, C_5H_5), 6.33 (1 H, pseudo q, C_5H_4), 6.30 (1 H, d, H_a), 6.16 (1 H, d, H_b), 6.11 (2 H, m, C_5H_4), 2.14 (3 H, s, Me), 1.97 (15 H, s, C_5Me_5), 1.95 (3 H, s, Me); δ_{C} (75.5 MHz, CD_2Cl_2 , room temp.) 142.6 [s, $\text{C}_{\text{ipso}}(\text{C}_5\text{H}_4)$], 130.5 (s, $\text{C}_{\text{g, h or i}}$), 129.1 (s, $\text{C}_{\text{g, h or i}}$), 128.3 (s, $\text{C}_{\text{g, h or i}}$), 125.5 (s, C_e), 125.15 (s, C_d), 125.1 (s, C_f), 125.0 (s, C_5Me_5), 123.7 (s, C_e), 118.2 (s, C_5H_4), 117.1 (s, C_a), 116.5 (s, C_5H_4), 116.3 (s, C_5H_5), 113.9 (s, C_5H_4), 112.4 (s, C_5H_4), 97.0 (s, C_b), 39.7 (s, CMe_2), 28.9 (s, Me), 27.2 (s, Me), 12.6 (s, C_5Me_5).

8; δ_{H} (300 MHz, CD_2Cl_2) 7.36 (1 H, m, H_c or f), 7.26 (1 H, m, H_c or f), 7.11 (2 H, m, H_d and e), 6.68 (1 H, pseudo q, C_5H_4), 6.51 (1 H, pseudo q, C_5H_4), 6.47 (1 H, pseudo q, C_5H_4 , partially obscured), 6.45 (5 H, s, C_5H_5), 6.20 (1 H, pseudo q, C_5H_4), 5.75 [1 H, pseudo t, $J(\text{HH}) = J(\text{RhH})$ 3, H_a], 5.60 (1 H, d, H_b), 2.08 (3 H, s, Me), 1.95 (3 H, s, Me); δ_{C} (75.5 MHz, CD_2Cl_2) 190.2 [d, $J(\text{RhC})$ 82, CO], 140.1 (s, C_{ipso}), 125.0 [d, $J(\text{CH})$ 161, C_d or e], 124.6 [d, $J(\text{CH})$ 161, C_d or e], 119.9 [d, $J(\text{CH})$ 161, C_c or f], 119.4 [d, $J(\text{CH})$ 164, C_c or f], 118.2 [d, $J(\text{CH})$ 176, C_5H_4], 117.6 (s, $\text{C}_{\text{g, h or i}}$), 116.9 [d, $J(\text{CH})$ 174, C_5H_4], 116.7 (s, $\text{C}_{\text{g, h or i}}$), 116.4 [d, $J(\text{CH})$ 176, C_5H_5], 114.8 [d, $J(\text{CH})$ 175, C_5H_4], 113.3 (s, $\text{C}_{\text{g, h or i}}$), 110.3 [d, $J(\text{CH})$ 182, C_5H_4], 97.8 [d, $J(\text{RhH})$ 6, C_a], 71.1 (s, C_b), 37.6 (s, CMe_2), 30.6 [q, $J(\text{CH})$ 127, Me(CH)], 30.4 [q, $J(\text{CH})$ 127, Me(CH)].

9; δ_{H} (300 MHz, CD_2Cl_2) 7.46 (2 H, pseudo t, H_c and f), 7.08 (2 H, m, H_d and e), 6.69 (1 H, br s, C_5H_4), 6.45 (5 H, s, C_5H_5), 6.45 (2 H, obscured, C_5H_4), 6.28 (1 H, br s, C_5H_4), 5.13 (1 H, br s, H_a), 4.66 (1 H, br s, H_b), 2.07 (3 H, s, Me), 1.93 (3 H, s, Me); δ_{C} (75.5 MHz, CD_2Cl_2) 225.3 (s, CO), 141.1 (s, C_{ipso}), 127.0 (s, C_d or e), 126.7 (s, C_d or e), 125.6 (s, C_c or f), 124.3 (s, C_c or f), 117.6 (s, C_5H_4), 117.0 (s, C_5H_4), 116.4 (s, C_5H_5), 113.6 (s, C_5H_4), 111.5 (s, C_5H_4), 105.3 (s, $\text{C}_{\text{g, h or i}}$), 104.3 (s, $\text{C}_{\text{g, h or i}}$), 101.2 (s, $\text{C}_{\text{g, h or i}}$), 89.1 (s, C_a), 69.8 (s, C_b), 37.6 (s, CMe_2), 30.8 (s, Me), 29.7 (s, Me).

\S Selected IR data: $\tilde{\nu}/\text{cm}^{-1}$ (KBr disc) for 8 $\nu(\text{CO})$ 2038s, 1985s; for 9 $\nu(\text{CO})$ 2012s, 1935s, 1920s.

References

- R. D. Adams, *Polyhedron*, 1988, **7**, 2251.
- K. P. Reddy and J. L. Petersen, *Organometallics*, 1989, **8**, 2107.
- D. W. Stephan, *Coord. Chem. Rev.*, 1989, **95**, 42.
- H. Werner, D. Schneider and M. Schulz, *Chem. Ber.*, 1992, **125**, 1017.
- I. E. Nifant'ev, M. V. Borzov, A. V. Churakov, S. G. Mkoyan and L. O. Atovmian, *Organometallics*, 1992, **11**, 3942.
- G. M. Diamond, M. L. H. Green, P. Mountford, N. A. Popham and A. N. Chernega, *J. Chem. Soc., Chem. Commun.*, 1994, 103.
- R. T. Baker and T. H. Tulip, *Organometallics*, 1986, **5**, 839.
- M. E. Rerek and F. Basolo, *J. Am. Chem. Soc.*, 1984, **106**, 5908.
- J. S. Rollet, *Computing Methods in Crystallography*, Pergamon Press, Oxford, 1965.
- N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
- D. J. Watkin, J. R. Carruthers and P. W. Betteridge, CRYSTALS user guide, Chemical Crystallography Laboratory, University of Oxford, 1985.