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SYNTHESES OF METAL CARBONYLS

XVII *. FORMATION OF A HETERONUCLEAR ORGANOMETALLIC CLUSTER CONTAINING RUTHENIUM AND RHODIUM; CRYSTAL AND MOLECULAR STRUCTURE OF $\{[Rh(\eta\text{-}C_5Me_5)]_3[Ru(CO)_3](\mu_3\text{-}CO)_2\}$

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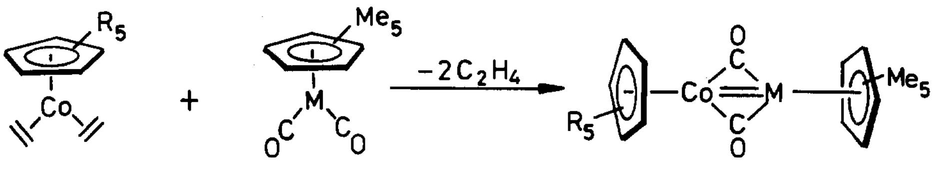
Summary

$Ru(C_6Me_6)(C_2H_4)_2$ reacts with $Rh(C_5Me_5)(CO)_2$ to give the known dinuclear complex $[Rh(C_5Me_5)(CO)]_2$ and the new heteronuclear cluster complex $\{[Rh(C_5Me_5)]_3[Ru(CO)_3](\mu_3\text{-}CO)_2\}$ which has been fully characterized by a single crystal X-ray diffraction study.

Introduction

The synthesis of heterodinuclear transition-metal complexes containing multiple metal–metal bonds as chemically reactive sites is a challenging task, but one which

SCHEME 1



1. 2. 3.

M = Rh,Ir ; R = H,Me

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* For part XVI see ref. 1.

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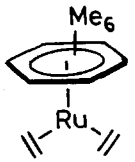
has been achieved for the cobalt triad using the methodology outlined in Scheme 1 [2,3]. This method utilizes the lability of the volatile ethylene ligands in the olefin complexes **1** to generate coordinatively unsaturated species which can then attack the dicarbonylmetal center in compounds **2** affording ultimately products **3**. These formally contain a heteronuclear metal–metal double bond, and have been used as precursors for bridging alkylidene compounds [2,3], and as building blocks for rational syntheses of new metal cluster complexes [3]. With a view to extending this methodology outside the cobalt triad we have attempted to replace the bis(ethylene) reactants **1** with the isoelectronic zerovalent ruthenium complex **4** [4], in the hope of producing the unsaturated ruthenium–rhodium complex **5**. However, the major product of this reaction is not **5** but the new cluster compound **7**, which represents a further addition to the tiny family of newly discovered heteronuclear metal clusters containing ruthenium–rhodium bonds.



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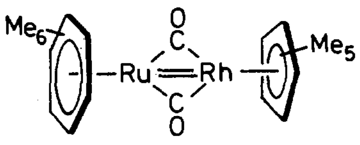

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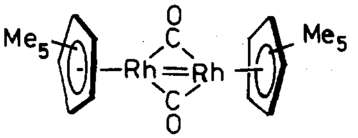

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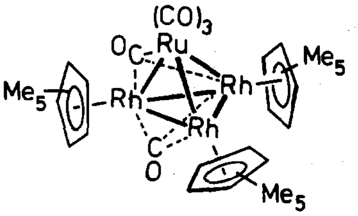


7.

Results and discussion

The reaction of **4** with excess [Rh(η-C_5Me_5)$(CO)_2$] proceeded smoothly in refluxing heptane to afford a deep violet solution. Evaporation followed by low temperature column chromatography of the residue afforded hexamethylbenzene, the known deep blue unsaturated homodinuclear complex **6** [5], and a purple band containing the cluster complex **7**. This complex was fully characterized spectroscopically and by a single crystal X-ray diffraction study. An ORTEP drawing of the structure of **7** including the atomic numbering scheme is shown in Fig. 1, a view of the tetranuclear core with the pentamethylcyclopentadienyl ligands omitted is illustrated in Fig. 2, and a molecular stereoview is presented in Fig. 3. Fractional atomic coordinates are listed in Table 1, and some important bond lengths and bond angles in Table 2.

Three clusters of the cobalt triad, complexes **8**, which are isolobal analogues of **7**, have been synthesized previously [3,6], but this generic cluster type has not been characterized crystallographically to date. Compound **7** appears to be only the

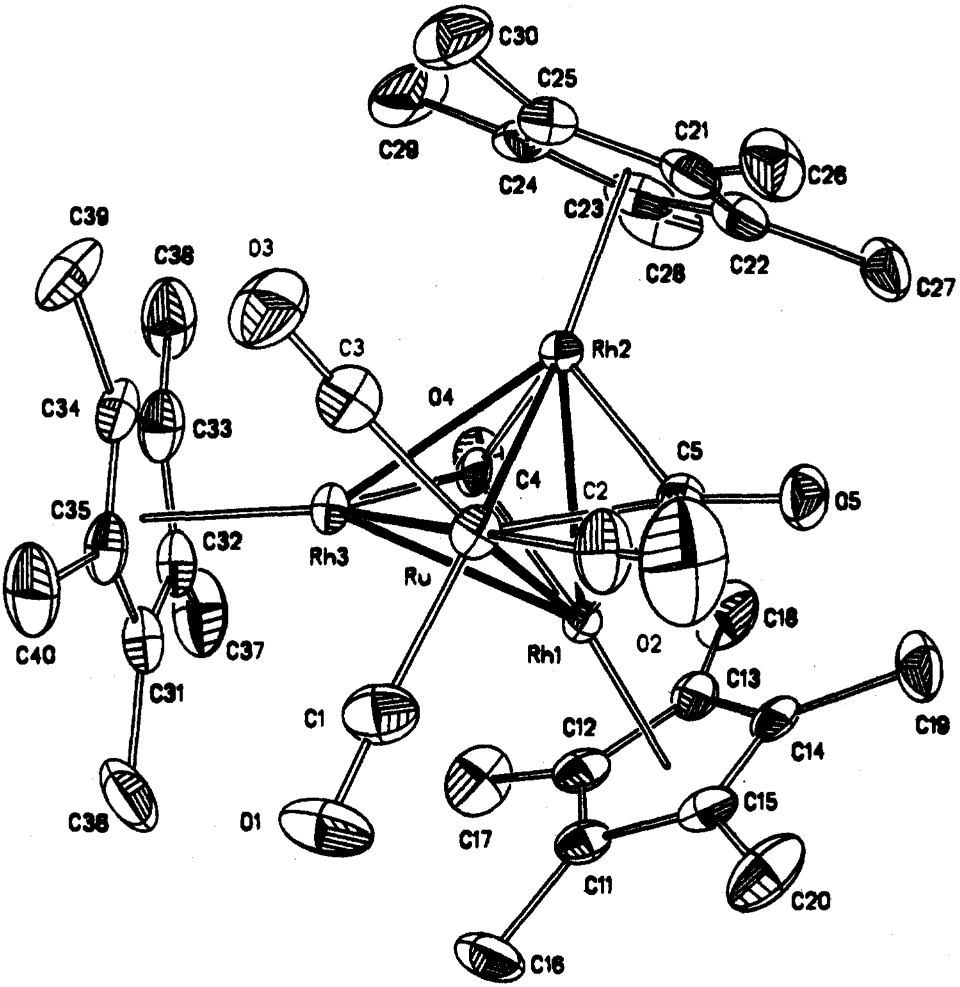
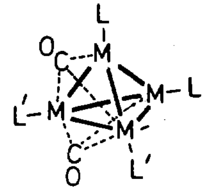


Fig. 1. Molecular structure and labelling scheme for complex 7 with 40% probability ellipsoids.

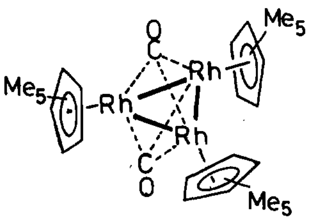
fourth structurally characterized example of a cluster containing Ru–Rh bonds, and is the first which incorporates either an organic π-ligand or triply bridging carbonyl ligands [7]. The previously characterized ruthenium–rhodium clusters are the neutral, tetranuclear, hydridocarbonyl complex $[H_2Ru_2Rh_2(CO)_{12}]$ [7a], the neutral pentanuclear compound $[Ru_3Rh_2(CO)_{13}(PEt_3)(\mu_3\text{-PPh})]$ [7b] and the pentanuclear dianion $[RuRh_4(CO)_{15}]^{2-}$ [7c].



8.

$M = M' = Co, Rh$; $L = L' = C_5H_5$

$M = Rh, M' = Co$; $L = C_9H_7, L' = C_5Me_5$



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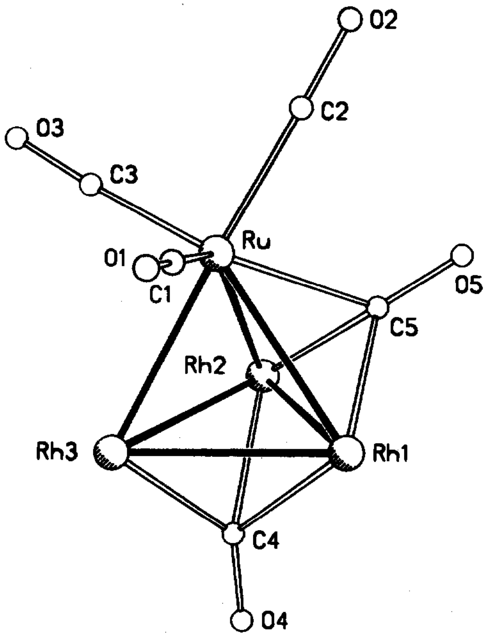

Fig. 2. View of the metal core of 7, including carbon monoxide ligands but excluding pentamethylcyclopentadienyl ligands.

The metal core of 7 consists of a flattened tetrahedron with the two shortest edges comprising the Rh(1)-Rh(2) and Ru-Rh(3) bonds. The triply bridging carbonyl ligands do not occupy equivalent faces of the cluster nor are they symmetrically bound to each metal atom on their respective cluster faces. Thus C(4) is significantly closer to Rh(3) (1.97(1) Å) than to Rh(1) (2.17(1) Å) or Rh(2) (2.14(1) Å), whereas C(5) is more closely associated with the two rhodium atoms Rh(1) (2.03(1) Å) and Rh(2) (2.05(1) Å) than with Ru (2.19(1) Å).

Since so few complexes containing Ru-Rh bonds have been structurally characterized some comments regarding the Rh-Ru bond distances are in order. However, comparisons with the few previously reported examples are not particularly rewarding; none of these other compounds contains a Ru-Rh bond as part of a

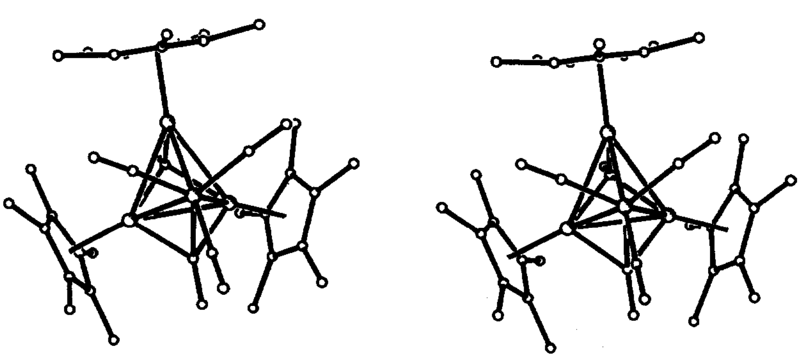

Fig. 3. Stereoview of the molecular structure of 7.

TABLE 1

ATOM COORDINATES ($\times 10^4$) AND TEMPERATURE FACTORS (Å^2 $\times 10^3$)

Atom	x	y	z	U [a]
Rh(1)	8240(1)	441	4603(1)	25(1)
Rh(2)	8139(1)	1870(1)	5002(1)	27(1)
Rh(3)	8375(1)	955(1)	6922(1)	28(1)
Ru	9498(1)	1183(1)	5378(1)	31(1)
O(1)	10195(6)	−216(6)	6309(13)	76(4)
O(2)	10748(7)	1446(10)	3506(13)	103(6)
O(3)	10153(7)	2324(7)	7045(11)	75(4)
O(4)	6807(4)	963(5)	5941(8)	39(3)
O(5)	8933(5)	1395(5)	2712(7)	47(3)
C(1)	9935(8)	316(8)	5986(15)	57(5)
C(2)	10284(8)	1341(9)	4185(13)	54(5)
C(3)	9889(7)	1872(8)	6423(12)	45(4)
C(4)	7478(6)	1024(6)	5838(9)	30(3)
C(5)	8762(7)	1288(6)	3763(11)	36(4)
C(11)	8352(7)	−761(6)	4416(12)	36(4)
C(12)	7555(8)	−609(7)	4602(12)	42(4)
C(13)	7289(8)	−183(7)	3619(12)	44(4)
C(14)	7924(8)	−77(7)	2823(11)	42(4)
C(15)	8577(8)	−420(7)	3309(12)	44(4)
C(16)	8861(9)	−1289(8)	5102(15)	62(6)
C(18)	6443(9)	79(10)	3453(16)	69(6)
C(19)	7830(10)	269(9)	1570(12)	59(5)
C(20)	9370(9)	−469(11)	2710(16)	72(6)
C(17)	7067(10)	−896(9)	5656(16)	69(6)
C(21)	8354(7)	2893(7)	3980(13)	45(4)
C(22)	7621(8)	2587(7)	3581(12)	44(4)
C(23)	7074(8)	2569(7)	4560(15)	51(5)
C(24)	7456(9)	2863(7)	5609(12)	49(5)
C(25)	8225(8)	3077(7)	5262(13)	48(5)
C(26)	9018(8)	3056(9)	3244(13)	57(5)
C(27)	7450(10)	2346(8)	2254(13)	61(5)
C(28)	6242(8)	2318(9)	4454(19)	69(6)
C(29)	7044(11)	2997(10)	6783(18)	82(7)
C(30)	8779(10)	3519(8)	6020(16)	68(6)
C(31)	8588(8)	182(8)	8487(11)	48(5)
C(32)	7791(8)	407(9)	8491(10)	47(4)
C(33)	7766(7)	1165(9)	8712(11)	50(5)
C(34)	8585(8)	1413(7)	8820(11)	41(4)
C(35)	9050(6)	791(8)	8694(11)	42(4)
C(36)	8847(11)	−616(10)	8466(16)	76(7)
C(37)	7071(10)	−66(12)	8487(16)	78(7)
C(38)	7049(10)	1633(12)	8942(15)	79(7)
C(39)	8824(11)	2158(9)	9213(15)	73(6)
C(40)	9909(8)	749(11)	8980(13)	70(6)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

triangular face triply-bridged by CO, and none contains a π-bonded organic ligand. We do note that all three Rh–Ru bonds in 7 are significantly shorter than any previously reported, the range in other complexes being 2.729(1)–3.005(1) Å [7]. The Ru–Rh(3) distance in 7 of 2.615(1) Å thus represents the shortest yet reported, a

TABLE 2

IMPORTANT BOND LENGTHS (Å) AND BOND ANGLES (°) FOR COMPOUND 7 (Numbers in parentheses refer to the esd's for the last digit. CNT = centroid of the pentamethylcyclopentadienyl ring.)

Rh(1)–Rh(2)	2.680(1)	Ru–C(1)	1.89(1)
Rh(1)–Rh(3)	2.730(1)	Ru–C(2)	1.91(1)
Rh(1)–Ru	2.711(1)	Ru–C(3)	1.84(1)
Rh(2)–Rh(3)	2.734(1)	Rh(1)–C(4)	2.17(1)
Rh(2)–Ru	2.705(1)	Rh(2)–C(4)	2.14(1)
Rh(3)–Ru	2.615(1)	Rh(3)–C(4)	1.97(1)
Rh(1)–CNT(1)	1.90(1)	Rh(1)–C(5)	2.03(1)
Rh(2)–CNT(2)	1.90(1)	Rh(2)–C(5)	2.05(1)
Rh(3)–CNT(3)	1.91(1)	Ru–C(5)	2.19(1)
Rh(1)–Rh(2)–Rh(3)	60.6(0)	CNT(1)–Rh(1)–C(4)	123.2(4)
Rh(1)–Rh(2)–Ru	60.5(0)	CNT(2)–Rh(2)–C(4)	124.6(4)
Rh(3)–Rh(2)–Ru	57.5(0)	CNT(3)–Rh(3)–C(4)	126.7(4)
Rh(2)–Rh(1)–Rh(3)	60.7(0)	CNT(1)–Rh(1)–C(5)	122.3(4)
Rh(2)–Rh(1)–Ru	60.2(0)	CNT(2)–Rh(2)–C(5)	120.6(4)
Rh(3)–Rh(1)–Ru	57.4(0)	C(1)–Ru–C(2)	94.9(7)
Rh(1)–Rh(3)–Rh(2)	58.8(0)	C(1)–Ru–C(3)	102.7(6)
Rh(1)–Rh(3)–Ru	60.9(0)	C(1)–Ru–C(5)	126.1(5)
Rh(2)–Rh(3)–Ru	60.7(0)	C(2)–Ru–C(3)	93.3(6)
Rh(1)–Ru–Rh(2)	59.3(0)	C(2)–Ru–C(5)	81.1(5)
Rh(1)–Ru–Rh(3)	61.6(0)	C(3)–Ru–C(5)	131.1(5)
Rh(2)–Ru–Rh(3)	61.8(0)		
Rh(1)–C(4)–Rh(2)	76.8(3)	Rh(1)–C(4)–Rh(3)	82.3(4)
Rh(1)–C(4)–Rh(3)	82.3(4)	Rh(2)–C(4)–Rh(3)	83.2(4)
Rh(1)–C(5)–Rh(2)	82.2(4)	Rh(1)–C(5)–Ru	79.8(4)
Rh(2)–C(5)–Ru	79.2(4)	Rh(1)–C(4)–O(4)	128.4(9)
Rh(2)–C(4)–O(4)	130.1(9)	Rh(3)–C(4)–O(4)	135.4(9)
Rh(1)–C(5)–O(5)	132.3(9)	Rh(2)–C(5)–O(5)	132.6(9)
Ru–C(5)–O(5)	130.3(9)		

rather curious observation because it is not CO-bridged, yet is significantly shorter than Ru–Rh(1) and Ru–Rh(2) which are both part of a triply bridged cluster face. A similar observation has been noted in the structure of the $[RuRh_4(CO)_{15}]^-$ anion [7c].

The distances of the three Rh atoms from the centroids of their respective pentamethylcyclopentadienyl rings are identical and unremarkable. In solution at room temperature the ^1H and $^{13}C\{^1H\}$ NMR spectra of 7 exhibit resonances for only one pentamethylcyclopentadienyl ring and one CO environment. Further studies of the dynamic NMR behavior of 7 will hopefully elucidate the mechanistic pathways for ligand site scrambling in this complex.

While the mechanism of formation of 7 is unclear, complex **4** presumably must act as a carbon monoxide abstractor, with displacement of both ethylene and hexamethylbenzene ligands. Formation of **6** from $[Rh(\eta\text{-}C_5Me_5)(CO)_2]$ does not proceed readily under the thermal conditions reported here, but high yields of **6** are produced in the presence of Me_3NO [5]. Formation of 7 can be envisaged to occur by addition of a $Ru(CO)_3$ fragment to the known trinuclear complex **9** [3], which could be formed under our reaction conditions.

Since rhodium and ruthenium are two of the most active transition metals in homogeneous catalytic reactions [8] the chemistry of their mixed cluster compounds will most likely prove to be significant. We hope that this mixed metal cluster will prove to be a useful entry point into the chemistry of tetranuclear clusters of this type.

Experimental

General procedures

Reactions were carried out under an atmosphere of dinitrogen which was deoxygenated over BASF catalyst and dried over P_4O_{10}. Hydrocarbon and ethereal solvents were dried by distillation from sodium or potassium benzophenone ketyl. Methylene chloride was distilled from P_4O_{10}. All solvents were stored and transferred under purified dinitrogen.

^{13}C and ^{1}H NMR spectra were obtained on a Varian XL-300 spectrometer; chemical shifts are reported in ppm downfield from internal tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer 599 spectrometer and calibrated against the 1601 cm^{-1} peak of polystyrene.

Microanalyses were performed by Spang, Eagle Harbor, Michigan.

Synthesis of complex 7

A mixture of complex **4** (0.205 g; 0.64 mmol) and $[Rh(\eta\text{-}C_5Me_5)(CO)_2]$ (0.400 g; 1.36 mmol) was refluxed in heptane (100 ml) for 4 h to afford a deep violet solution. Evaporation under vacuum followed by column chromatography of the residue (1 × 40 cm silica gel column at $-35°C$) afforded, in order of elution, a pale yellow band containing hexamethylbenzene (0.090 g; 86%), a deep blue band containing the known unsaturated homodinuclear complex **6** (0.098 g; 27%) [5], and a purple band containing the cluster complex **7** (0.286 g; 66%). [Yields of **6** and **7** based on Rh starting material]. Found: C, 44.06; H, 4.79. $C_{35}H_{45}O_5Rh_3Ru$ calcd.: C, 43.99; H, 4.75%. IR(hexane) ν(CO) 2000, 1950, 1932, 1690, 1665 cm^{-1}, ^{1}H NMR (C_6D_6) δ 1.66(s) ppm; ^{13}C NMR ($CDCl_3$, 20°C) δ 197.9(CO), 101.3(d, J(Rh-C) 2.7, C_5Me_5), 9.7(C_5Me_5) ppm. FD mass spectrum m/e 956 (P^+).

X-Ray diffraction studies

A red-black crystal (0.05 × 0.31 × 0.31 mm), grown from hexane, was found by photographic evidence and systematic absences to belong to either of the orthorhombic space groups, $Pn2_1a$ (nonstandard setting of $Pna2_1$) or $Pnma$: a 17.316(5), b 18.463(5), c 10.987(2) Å, V 3512.6(17) $Å^3$, $Z = 4$, ρ(calcd.) 1.807 g cm^{-3}, μ 17.90 cm^{-1} (Mo-K_α). Of 3492 absorption corrected reflections collected (Nicolet P3 Diffractometer $4° \leq 2\theta \leq 50°$, 23°C), 3193 were unique, and those 3056 considered observed ($F_0 \geq 3\sigma(F_0)$) were used in the solution (direct methods) and refinement (blocked cascade) of the structure. The choice of the non-centrosymmetric space group alternative $Pn2_1a$, which was initially suggested by the statistical distribution of E values, was later confirmed by the chemically reasonable solution and refinement of the structure. Nonetheless, due to the presence of a potential and correctly positioned crystallographic mirror plane defined by Ru, Rh(3), C(2), O(2), C(4), O(4), C(5), and O(5) processing of the data in the space group $Pnma$ was pursued; this led to chemically unreasonable ranges for bond parameters among closely related sets and was rejected. In the final stages of refinement all atoms were treated anisotropically. Since fewer than half of the hydrogen atoms were located on the final difference map, no attempt was made to incorporate hydrogens as either found or idealized contributions. At convergence, $R(F) = 0.0467$, $R_w(F) = 0.0460$, GOF = 1.487, and the highest peak on the final difference map, 0.97 $e\text{Å}^{-3}$, was located within the Rh_3Ru tetrahedron *.

Acknowledgements

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References

1 J.D. Korp, I. Bernal, W.A. Herrmann, and R. Serrano, Chem. Ber. 117 (1984) 434.
2 (a) W.A. Herrmann, C.E. Barnes, R. Serrano, and B. Kombouris, J. Organomet. Chem., 256 (1983) C30; (b) W.A. Herrmann, C.E. Barnes, Th. Zahn, and M.L. Ziegler, Organometallics, 4 (1985) 172.
3 M. Green, D.R. Hankey, J.A.K. Howard, P. Louca, and F.G.A. Stone, J. Chem. Soc. Chem. Commun., (1983) 757.
4 M.A. Bennett, T.-N. Huang, T.W. Matheson, and A.K. Smith, Inorg. Synth., 21 (1982) 76.
5 (a) A. Nutton, and P.M. Maitlis, J. Organomet. Chem., 166 (1979) C21; (b) N.M. Boag, M. Green, R.M. Mills, G.N. Pain, F.G.A. Stone, and P. Woodward, J. Chem. Soc. Chem. Commun., (1980) 1171; (c) W.A. Herrmann, Ch. Bauer, J. Plank, W. Kalcher, D. Speth, and M.L. Ziegler, Angew. Chem. Intern. Ed. Engl., 20 (1981) 193.
6 (a) K.P.C. Vollhardt, J.E. Bercaw, and R.G. Bergman, J. Organomet. Chem., 97 (1975) 283; (b) R.J. Lawson and J.R. Shapley, J. Am. Chem. Soc., 98 (1976) 7433.
7 (a) J. Pursiainen and T.A. Pakkanen, J. Chem. Soc. Chem. Commun., (1984) 252; (b) M.J. Mays, P.R. Raithby, P.L. Taylor, and K. Henrick, J. Chem. Soc. Dalton Trans., (1984) 959; (c) A. Fumagalli and G. Ciani, J. Organomet. Chem., 272 (1984) 91.
8 G. Wilkinson, F.G.A. Stone, and E.W. Abel (Eds), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982; Ruthenium (M.A. Bennett and M.I. Bruce: Volume 4, Chapter 32); Rhodium (R.P. Hughes: Volume 5, Chapter 35).

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* *Supplementary materials available.* Anisotropic temperature factors (Table 1S; 1 page), observed and calculated structure factors (Table 2S; 18 pages), and complete listings of all bond lengths (Table 3S; 1 page) and bond angles (Table 4S; 3 pages) for complex 7. This material can be obtained on request from the author (R.P.H.).