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Synthesis and Crystal Structure of the Novel Platinum-Bridged Hexaruthenium Alkynyl Cluster $Pt[Ru_3(\mu\text{-}H)\{\mu_4\text{-}\eta^2\text{-}C{\equiv}C(t\text{-}Bu)\}(CO)_9]_2$: Evidence for the Racemization of the Chiral Metal Framework

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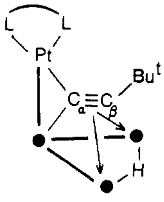
The cluster $Ru_3Pt(\mu\text{-}H)\{\mu_4\text{-}\eta^2\text{-}C{\equiv}C(t\text{-}Bu)\}(CO)_9(COD)$ decomposes in dichloromethane or toluene solution by elimination of a Pt atom and COD, affording orange crystals of the title complex $Pt[Ru_3(\mu\text{-}H)\{\mu_4\text{-}\eta^2\text{-}C{\equiv}C(t\text{-}Bu)\}(CO)_9]_2$ (**5**) in 40–50% yield. Crystal data for **5**: triclinic, space group $P\bar{1}$; $a = 9.546$ (2), $b = 12.993$ (2), $c = 17.786$ (2) Å; $\alpha = 72.97$ (1), $\beta = 82.48$ (1), $\gamma = 74.62$ (2)°; $V = 2030.4$ (6) Å^3; $Z = 2$; final R (R_w) values 0.033 (0.038) for 4806 independent observed ($I > 3.0\sigma(I)$) data. Complex **5** contains two Ru_3 cluster units linked by a "naked" Pt atom, with each cluster unit bonded via one Ru atom and the α-carbon of the alkynyl ligand. Variable-temperature ^{13}C NMR spectra show that the chiral metal framework undergoes racemization with an estimated $\Delta G^{\ddagger}_{266}$ of 57.1 (±1.1) kJ mol^{-1}.

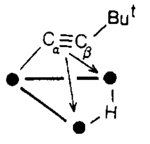
Introduction

We recently reported[1] the synthesis and crystal structure of the spiked triangular alkynyl cluster $Ru_3Pt(\mu\text{-}H)\{\mu_4\text{-}\eta^2\text{-}C{\equiv}C(t\text{-}Bu)\}(CO)_9(COD)$ (**1**) (COD = cycloocta-1,5-diene), which has a labile COD ligand coordinated to the Pt atom. Treatment of this cluster with CO results[1] in cleavage of the Pt–Ru bond and regeneration of the precursor alkynyl complex $Ru_3(\mu\text{-}H)\{\mu_3\text{-}\eta^2\text{-}C{\equiv}C(t\text{-}Bu)\}(CO)_9$ (**2**),[2] while with PPh_3 the phosphine-substituted complex $Ru_3(\mu\text{-}H)\{\mu_3\text{-}\eta^2\text{-}C{\equiv}C(t\text{-}Bu)\}(CO)_8(PPh_3)$[3] is formed as the major isolable product.[4] However reaction with diphosphine ligands (L_2) leaves the Ru_3Pt framework intact, initially forming the alkynyl clusters $Ru_3Pt(\mu\text{-}H)\{\mu_4\text{-}\eta^2\text{-}C{\equiv}C(t\text{-}Bu)\}(CO)_9(L_2)$ (**3**) (L_2 = bis(diphenylphosphino)ethane,[1] (2*S*,3*S*)-bis(diphenylphosphino)butane,[4] or (2*R*)-bis(diphenylphosphino)propane),[4] which rearrange at varying rates to the isomeric vinylidene complexes $Ru_3Pt\{\mu_4\text{-}\eta^2\text{-}C{=}C(H)\text{-}t\text{-}Bu\}(CO)_9(L_2)$.[1,4]



1 L⌒L = COD

3 L⌒L = dppe



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● = Ru(CO)$_3$

Due to the lability of the COD ligand, complex **1** is a potential synthon for higher nuclearity clusters. The reaction of **1** with $Os_3(\mu\text{-}H)_2(CO)_{10}$ (**4**) was therefore investigated, since it is known[5] that **4** reacts readily with the Pt–olefin complex $Pt(C_2H_4)_2(PR_3)$ affording $Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR_3)$.[5] The formation of an Os_3PtRu_3 cluster was anticipated, but instead Pt–Ru bond rupture and transfer of the Pt(COD) unit occurred, forming the cluster $Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_9(COD)$[6] together with **2**. Herein is reported the synthesis and characterization of the novel platinum-bridged cluster $Pt[Ru_3(\mu\text{-}H)\{\mu_4\text{-}\eta^2\text{-}C{\equiv}C(t\text{-}Bu)\}(CO)_9]_2$ (**5**), which demonstrates that the linking of two trinuclear clusters by a "naked" Pt atom is feasible. This cluster results from the formal self-condensation of **1** by elimination of a Pt atom and 2 mol of COD.

Results and Discussion

Solutions of complex **1** in dichloromethane or toluene are unstable at ambient temperatures in the absence of small amounts of free COD, slowly darkening due to the formation of colloidal Pt metal and depositing orange crystals of the title complex **5**. ^1H NMR studies on the course of this reaction showed that complex **2** is also formed, at a rate greater than the formation of **5**. In the presence of equimolar amounts of complex **2**, enhanced rates of formation of **5** were observed, with only slow loss of **2**. No signals attributable to $Pt(COD)_2$[7] were observed in either experiment. These data suggest that **1** decomposes via two pathways, one resulting in complex **2**, Pt metal, and COD and the other in an activated species, perhaps "$PtRu_3(\mu\text{-}H)\{C{\equiv}C(t\text{-}Bu)\}(CO)_9$" which then reacts with a further molecule of **2** forming complex **5**. Complex **5** can also be synthesized directly by treatment of a 2 molar excess of complex **2** with $Pt(C_2H_4)_3$,[7] which acts as a source of "naked" Pt. However overall yields are not substantially higher. Complex **5** has been characterized by a single-crystal X-ray diffraction study and spectroscopic techniques.

Crystal Structure of Complex 5. The molecular structure and atomic labeling scheme are shown in Figure 1, and atomic coordinates and selected metrical parameters given in Tables I and II, respectively. The structure consists of two $Ru_3(\mu\text{-}H)\{C{\equiv}C(t\text{-}Bu)\}(CO)_9$ units linked by a "naked" four-coordinate Pt atom, such that the cluster has overall approximate C_2 symmetry. The geometry of the spiked triangular $Ru_3Pt\{C{\equiv}C(t\text{-}Bu)\}$ core in each subunit closely resembles that found[1] in the clusters **1** and **3** (L_2 = dppe). The C_α carbon C(1) [C(4)][8] of the alkynyl

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[1] Ewing, P.; Farrugia, L. J. *Organometallics* **1989**, *8*, 1246.

[2] (a) Catti, M.; Gervasio, G.; Mason, S. A. *J. Chem. Soc., Dalton Trans.* **1977**, 2260. (b) Sappa, E.; Gambino, O.; Milone, L.; Cetini, G. *J. Organomet. Chem.* **1972**, *39*, 169.

[3] Jangala, C.; Rosenberg, E.; Skinner, D.; Aime, S.; Milone, L. *Inorg. Chem.* **1980**, *19*, 1571.

[4] Farrugia, L. J.; MacDonald, N. M.; Peacock, R. D., unpublished results.

[5] Farrugia, L. J.; Howard, J. A. K.; Mitrprachachon, P.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1981**, 155.

[6] Ewing, P.; Farrugia, L. J. *J. Organomet. Chem.* **1988**, *347*, C31.

[7] (a) Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 271. (b) Spencer, J. L. *Inorg. Synth.* **1979**, *19*, 213.

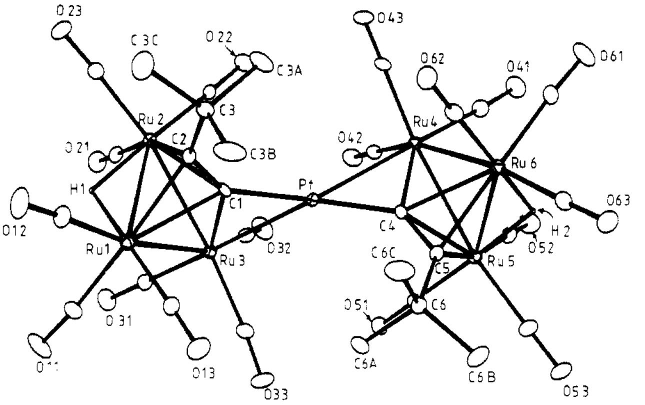

Figure 1. Molecular structure of complex **5**, showing the atomic labeling scheme. Thermal ellipsoids are drawn at the 10% probability level and H atoms shown as arbitary spheres.

ligand is formally σ-bonded to the Ru(3) [Ru(4)] center (C(1)–Ru(3) = 2.109 (9) [C(4)–Ru(4) = 2.068 (10)] Å) and to the Pt atom (C(1)–Pt = 1.997 (9) [C(4)–Pt = 2.001 (10)] Å). As found in complexes **1** and **3**,[1] the alkynyl unit is asymmetrically π-bonded to the remaining Ru atoms, such that the Δ_α and Δ_β values[9] are 0.111 and 0.040 [0.071 and 0.042] Å, respectively, and the angle between the C(1)–C(2) [C(3)–C(4)] axis and the Ru(1)–Ru(2) [Ru(5)–Ru(6)] vector is 95.3 [93.8]°. The slight differences between the values of these parameters in the two subunits is a reflection of the flexibility of the μ_4-η^2-alkynyl coordination mode. This has been discussed in some detail for complexes **1** and **3** where, for comparison, the Δ_α and Δ_β values are respectively 0.193 and 0.042 Å for **1** and 0.031 and 0.004 Å for **3**.[1]

Table I. Final Positional Parameters (Fractional Coordinates) with Esd's in Parentheses and Isotropic Thermal Parameters (Å^2) (Equivalent Isotropic Parameters U_{eq} for Anisotropic Atoms) for $Pt[Ru_3(\mu\text{-}H)\{\mu_4\text{-}\eta^2\text{-}C{\equiv}C(t\text{-}Bu)\}(CO)_9]_2$ (5)[a]

	x/a	y/b	z/c	U_{eq}
Pt	0.77183 (4)	0.03084 (3)	0.28523 (2)	0.032
Ru(1)	0.73243 (10)	0.31391 (7)	0.09293 (4)	0.041
Ru(2)	0.49712 (9)	0.30279 (6)	0.20622 (5)	0.038
Ru(3)	0.78098 (9)	0.24474 (6)	0.25534 (4)	0.037
Ru(4)	0.72523 (9)	−0.14785 (6)	0.39864 (4)	0.034
Ru(5)	1.02798 (9)	−0.22356 (7)	0.40881 (4)	0.038
Ru(6)	0.88144 (9)	−0.31417 (6)	0.32648 (5)	0.040
O(11)	0.8605 (13)	0.5171 (8)	0.0640 (6)	0.113
O(12)	0.6188 (12)	0.3952 (7)	−0.0708 (5)	0.092
O(13)	1.0250 (11)	0.1785 (8)	0.0452 (5)	0.091
O(21)	0.4355 (11)	0.4832 (7)	0.2919 (5)	0.087
O(22)	0.3710 (9)	0.1532 (7)	0.3481 (5)	0.072
O(23)	0.2127 (10)	0.3946 (8)	0.1213 (6)	0.093
O(31)	0.7758 (11)	0.4828 (7)	0.2417 (5)	0.088
O(32)	0.7295 (13)	0.2150 (8)	0.4321 (5)	0.105
O(33)	1.1126 (10)	0.1797 (8)	0.2504 (6)	0.089
O(41)	0.6660 (11)	−0.3265 (8)	0.5429 (5)	0.089
O(42)	0.6517 (10)	0.0194 (7)	0.4947 (5)	0.075
O(43)	0.4212 (9)	−0.1045 (7)	0.3452 (5)	0.076
O(51)	1.0832 (10)	−0.0073 (7)	0.4156 (4)	0.070
O(52)	0.9765 (11)	−0.2986 (8)	0.5866 (5)	0.093
O(53)	1.3509 (10)	−0.3484 (8)	0.4136 (5)	0.088
O(61)	0.7104 (12)	−0.4812 (8)	0.4249 (6)	0.105
O(62)	0.6823 (11)	−0.2509 (7)	0.1917 (5)	0.089
O(63)	1.1007 (10)	−0.4947 (7)	0.2675 (6)	0.095
C(1)	0.6898 (10)	0.1604 (7)	0.1969 (5)	0.034
C(2)	0.6102 (11)	0.1856 (7)	0.1356 (5)	0.039
C(3)	0.5573 (13)	0.1166 (9)	0.0947 (6)	0.052
C(3A)	0.4924 (16)	0.0310 (11)	0.1569 (7)	0.085
C(3B)	0.6797 (16)	0.0611 (12)	0.0504 (9)	0.103
C(3C)	0.439 (2)	0.184 (1)	0.038 (1)	0.126
C(4)	0.8823 (11)	−0.1280 (7)	0.3073 (5)	0.037
C(5)	1.0076 (11)	−0.1901 (8)	0.2808 (5)	0.040
C(6)	1.1080 (12)	−0.1656 (8)	0.2082 (6)	0.046
C(6A)	1.1359 (14)	−0.0523 (10)	0.1957 (7)	0.073
C(6B)	1.2557 (14)	−0.2471 (11)	0.2155 (8)	0.082
C(6C)	1.0386 (15)	−0.1645 (13)	0.1387 (7)	0.091
C(11)	0.8201 (14)	0.4395 (10)	0.0754 (6)	0.063
C(12)	0.6579 (14)	0.3643 (9)	−0.0100 (7)	0.060
C(13)	0.9134 (14)	0.2266 (10)	0.0620 (6)	0.059
C(21)	0.4594 (13)	0.4161 (9)	0.2606 (7)	0.056
C(22)	0.4209 (12)	0.2085 (8)	0.2935 (6)	0.046
C(23)	0.3176 (14)	0.3577 (10)	0.1533 (7)	0.060
C(31)	0.7793 (13)	0.3919 (9)	0.2452 (7)	0.062
C(32)	0.7490 (13)	0.2194 (10)	0.3664 (7)	0.060
C(33)	0.9901 (14)	0.1990 (10)	0.2531 (7)	0.063
C(41)	0.6910 (13)	−0.2618 (10)	0.4893 (6)	0.056
C(42)	0.6773 (12)	−0.0422 (9)	0.4567 (6)	0.048
C(43)	0.5336 (13)	−0.1206 (9)	0.3642 (6)	0.049
C(51)	1.0641 (12)	−0.0887 (9)	0.4114 (6)	0.050
C(52)	0.9929 (12)	−0.2690 (9)	0.5203 (6)	0.055
C(53)	1.2307 (14)	−0.3008 (11)	0.4107 (6)	0.062
C(61)	0.7702 (14)	−0.4165 (9)	0.3892 (7)	0.062
C(62)	0.7570 (13)	−0.2740 (9)	0.2420 (7)	0.059
C(63)	1.0188 (14)	−0.4259 (9)	0.2881 (7)	0.061
H(1)	0.57270	0.39320	0.12790	0.050
H(2)	0.98780	−0.34680	0.40720	0.050

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

The geometry about the Pt atom is probably best described as very distorted tetrahedral, with an angle of 96.8° between the Pt–Ru(3)–C(1) and Pt–Ru(4)–C(4) planes and angles about the Pt atom in the range 49.7 (3)–147.5 (3)° (see Table II). The MPT–Pt–MPT angle is 175.5° (MPT is midpoint of the Pt-bridged Ru–C vectors). Complexes containing cluster subunits linked by "naked" post-transition metals of groups 11 or 12;[10] e.g. Cu,[11] Ag,[12] Au,[11,13] or Hg[13b,14] are relatively familiar, but examples with "naked" group 10 metals are less common. The complexes $Pt[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]_2$[15] and $[Pt\{Fe_2(CO)_8\}_2]^{2-}$[16] contain Pt-linked metal dimers, the former having a pseudotetrahedral, formally d^{10} Pt(0) center and the latter a pseudo-square-planar d^8 Pt(II) center. Stone and coworkers have synthesized numerous chain[17] and "star"[17c,18]

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[8] Atoms or parameters in brackets indicate corresponding atoms or parameters in the other cluster subunit.

[9] $\Delta_{\alpha(\beta)} = |(M(2)\text{–}C_{\alpha(\beta)}) - (M(3)\text{–}C_{\alpha(\beta)})|$ where M(2) and M(3) are the two Ru atoms π-bonded to the alkynyl ligand.

[10] In this paper, the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

[11] Hallam, M. F.; Mingos, D. M. P.; Adatia, T.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1988**, 335.

[12] (a) Albinati, A.; Dahmen, K.-H.; Togni, A.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 766. (b) Fajardo, M.; Gomez-Sal, M. P.; Holden, H. D.; Johnson, B. F. G.; Lewis, J.; McQueen, R. C. S.; Raithby, P. R. *J. Organomet. Chem.* **1984**, *267*, C25. (c) Heaton, B. T.; Strona, L.; Martinengo, S.; Strumbolo, D.; Albano, V. G.; Braga, D. *J. Chem. Soc., Dalton Trans.* **1983**, 2175.

[13] (a) Johnson, B. F. G.; Kaner, D. A.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1981**, 753. (b) Drake, S. R.; Hendrick, K.; Johnson, B. F. G.; McPartlin, M. *J. Chem. Soc., Chem. Commun.* **1986**, 928.

[14] (a) Gomez-Sal, M. P.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Syed-Mustaffa, S. N. A. B. *J. Organomet. Chem.* **1984**, *273*, C21. (b) Braunstein, P.; Rosé, J.; Tiripicchio, A.; Tiripicchio Camellini, M. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 767. (c) Ermer, S.; King, K.; Hardcastle, K. I.; Rosenberg, E.; Manotti Landfredi, A. M.; Tiripicchio, A.; Tiripicchio Camellini, M. *Inorg. Chem.* **1982**, *22*, 1339. (d) Farrugia, L. J. *J. Chem. Soc., Chem. Commun.* **1987**, 147. (e) Yamamoto, Y.; Yamazaki, H.; Sukurai, T. *J. Am. Chem. Soc.* **1982**, *104*, 2329. (f) Albinati, A.; Moor, A.; Pregosin, P. S.; Venanzi, L. M. *Ibid.* **1982**, *104*, 7672.

[15] Green, M.; Howard, J. A. K.; Pain, G. N.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1982**, 1327.

[16] Longoni, G.; Manassero, M.; Sansoni, M. *J. Am. Chem. Soc.* **1980**, *102*, 3242.

Table II. Selected Bond Lengths (Å) and Bond Angles (deg) for $Pt[Ru_3(\mu\text{-}H)\{\mu_4\text{-}\eta^2\text{-}C{\equiv}C(t\text{-}Bu)\}(CO)_9]_2$ (5)

Bond Lengths							
Pt–Ru(3)	2.695 (1)	Pt–Ru(4)	2.688 (1)	Ru(4)–Ru(6)	2.820 (2)	Ru(4)–C(4)	2.068 (10)
Pt–C(1)	1.997 (9)	Pt–C(4)	2.001 (10)	Ru(4)–C(41)	1.903 (12)	Ru(4)–C(42)	1.880 (11)
Ru(1)–Ru(2)	2.818 (2)	Ru(1)–Ru(3)	2.824 (1)	Ru(4)–C(43)	1.915 (12)	Ru(5)–Ru(6)	2.812 (2)
Ru(1)–C(1)	2.375 (9)	Ru(1)–C(2)	2.185 (10)	Ru(5)–C(4)	2.273 (9)	Ru(5)–C(5)	2.214 (9)
Ru(1)–C(11)	1.954 (13)	Ru(1)–C(12)	1.918 (11)	Ru(5)–C(51)	1.888 (11)	Ru(5)–C(52)	1.907 (11)
Ru(1)–C(13)	1.910 (14)	Ru(2)–Ru(3)	2.797 (2)	Ru(5)–C(53)	1.929 (13)	Ru(6)–C(4)	2.344 (9)
Ru(2)–C(1)	2.264 (10)	Ru(2)–C(2)	2.225 (10)	Ru(6)–C(5)	2.172 (10)	Ru(6)–C(61)	1.926 (13)
Ru(2)–C(21)	1.922 (11)	Ru(2)–C(22)	1.871 (11)	Ru(6)–C(62)	1.903 (12)	Ru(6)–C(63)	1.906 (13)
Ru(2)–C(23)	1.926 (13)	Ru(3)–C(1)	2.109 (9)	C(1)–C(2)	1.322 (13)	C(2)–C(3)	1.519 (13)
Ru(3)–C(31)	1.863 (11)	Ru(3)–C(32)	1.902 (12)	C(4)–C(5)	1.367 (14)	C(5)–C(6)	1.510 (15)
Ru(3)–C(33)	1.925 (14)	Ru(4)–Ru(5)	2.807 (2)	C–O(carbonyl)	1.14 (2)[a]		

Bond Angles							
Ru(3)–Pt–Ru(4)	144.3 (1)	Ru(3)–Pt–C(1)	50.8 (3)	Ru(6)–Ru(4)–C(43)	101.5 (4)	C(4)–Ru(4)–C(41)	137.3 (5)
Ru(3)–Pt–C(4)	147.5 (3)	Ru(4)–Pt–C(1)	146.9 (3)	C(4)–Ru(4)–C(42)	117.1 (5)	C(4)–Ru(4)–C(43)	113.6 (5)
Ru(4)–Pt–C(4)	49.7 (3)	C(1)–Pt–C(4)	141.6 (4)	C(41)–Ru(4)–C(42)	91.5 (5)	C(41)–Ru(4)–C(43)	92.4 (5)
Ru(2)–Ru(1)–Ru(3)	59.4 (1)	Ru(2)–Ru(1)–C(1)	50.8 (3)	C(42)–Ru(4)–C(43)	95.9 (5)	Ru(4)–Ru(5)–Ru(6)	60.3 (1)
Ru(2)–Ru(1)–C(2)	50.9 (3)	Ru(2)–Ru(1)–C(11)	116.5 (4)	Ru(4)–Ru(5)–C(4)	46.6 (3)	Ru(4)–Ru(5)–C(5)	78.8 (3)
Ru(2)–Ru(1)–C(12)	108.7 (4)	Ru(2)–Ru(1)–C(13)	142.0 (4)	Ru(4)–Ru(5)–C(51)	96.9 (4)	Ru(4)–Ru(5)–C(52)	87.3 (4)
Ru(3)–Ru(1)–C(1)	46.9 (3)	Ru(3)–Ru(1)–C(2)	78.6 (3)	Ru(4)–Ru(5)–C(53)	168.6 (4)	Ru(6)–Ru(5)–C(4)	53.6 (3)
Ru(3)–Ru(1)–C(11)	92.2 (4)	Ru(3)–Ru(1)–C(12)	168.1 (4)	Ru(6)–Ru(5)–C(5)	49.5 (3)	Ru(6)–Ru(5)–C(51)	142.5 (4)
Ru(3)–Ru(1)–C(13)	95.5 (4)	C(1)–Ru(1)–C(2)	33.4 (4)	Ru(6)–Ru(5)–C(52)	113.6 (4)	Ru(6)–Ru(5)–C(53)	109.0 (4)
C(1)–Ru(1)–C(11)	139.1 (4)	C(1)–Ru(1)–C(12)	127.1 (5)	C(4)–Ru(5)–C(5)	35.4 (4)	C(4)–Ru(5)–C(51)	88.9 (4)
C(1)–Ru(1)–C(13)	91.2 (5)	C(2)–Ru(1)–C(11)	167.1 (5)	C(4)–Ru(5)–C(52)	133.6 (5)	C(4)–Ru(5)–C(53)	131.6 (4)
C(2)–Ru(1)–C(12)	94.0 (5)	C(2)–Ru(1)–C(13)	99.4 (5)	C(5)–Ru(5)–C(51)	100.0 (4)	C(5)–Ru(5)–C(52)	162.1 (5)
C(11)–Ru(1)–C(12)	93.5 (5)	C(11)–Ru(1)–C(13)	90.4 (6)	C(5)–Ru(5)–C(53)	97.0 (5)	C(51)–Ru(5)–C(52)	92.8 (5)
C(12)–Ru(1)–C(13)	94.9 (5)	Ru(1)–Ru(2)–Ru(3)	60.4 (1)	C(51)–Ru(5)–C(53)	94.2 (6)	C(52)–Ru(5)–C(53)	94.5 (5)
Ru(1)–Ru(2)–C(1)	54.4 (3)	Ru(1)–Ru(2)–C(2)	49.6 (3)	Ru(4)–Ru(6)–Ru(5)	59.8 (1)	Ru(4)–Ru(6)–C(4)	46.1 (3)
Ru(1)–Ru(2)–C(21)	113.2 (4)	Ru(1)–Ru(2)–C(22)	143.8 (4)	Ru(4)–Ru(6)–C(5)	79.2 (3)	Ru(4)–Ru(6)–C(61)	91.4 (4)
Ru(1)–Ru(2)–C(23)	109.1 (4)	Ru(3)–Ru(2)–C(1)	47.8 (3)	Ru(4)–Ru(6)–C(62)	96.2 (4)	Ru(4)–Ru(6)–C(63)	168.6 (4)
Ru(3)–Ru(2)–C(2)	78.6 (3	Ru(3)–Ru(2)–C(21)	86.2 (4)	Ru(5)–Ru(6)–C(4)	51.3 (3)	Ru(5)–Ru(6)–C(5)	50.8 (3)
Ru(3)–Ru(2)–C(22)	96.8 (4)	Ru(3)–Ru(2)–C(23)	168.9 (4)	Ru(5)–Ru(6)–C(61)	116.6 (4)	Ru(5)–Ru(6)–C(62)	142.1 (4)
C(1)–Ru(2)–C(2)	34.2 (4)	C(1)–Ru(2)–C(21)	133.7 (5)	Ru(5)–Ru(6)–C(63)	108.9 (4)	C(4)–Ru(6)–C(5)	35.0 (4)
C(1)–Ru(2)–C(22)	89.5 (4)	C(1)–Ru(2)–C(23)	130.6 (5)	C(4)–Ru(6)–C(61)	137.3 (5)	C(4)–Ru(6)–C(62)	90.8 (4)
C(2)–Ru(2)–C(21)	161.4 (5)	C(2)–Ru(2)–C(22)	101.5 (4)	C(4)–Ru(6)–C(63)	129.3 (5)	C(5)–Ru(6)–C(61)	167.0 (5)
C(2)–Ru(2)–C(23)	97.4 (5)	C(21)–Ru(2)–C(22)	90.8 (5)	C(5)–Ru(6)–C(62)	99.1 (5)	C(5)–Ru(6)–C(63)	94.6 (5)
C(21)–Ru(2)–C(23)	95.5 (5)	C(22)–Ru(2)–C(23)	94.2 (5)	C(61)–Ru(6)–C(62)	90.7 (6)	C(61)–Ru(6)–C(63)	93.1 (5)
Pt–Ru(3)–Ru(1)	98.9 (1)	Pt–Ru(3)–Ru(2)	87.7 (1)	C(62)–Ru(6)–C(63)	94.2 (5)	Pt–C(1)–Ru(1)	147.2 (5)
Pt–Ru(3)–C(1)	47.2 (3)	Pt–Ru(3)–C(31)	174.1 (4)	Pt–C(1)–Ru(2)	126.4 (5)	Pt–C(1)–Ru(3)	82.0 (4)
Pt–Ru(3)–C(32)	84.2 (4)	Ru(1)–Ru(3)–Ru(2)	60.2 (1)	Pt–C(1)–C(2)	140.3 (7)	Ru(1)–C(1)–Ru(2)	74.8 (3)
Ru(1)–Ru(3)–C(1)	55.3 (3)	Ru(1)–Ru(3)–C(31)	86.1 (4)	Ru(1)–C(1)–Ru(3)	77.8 (3)	Ru(1)–C(1)–C(2)	65.4 (6)
Ru(1)–Ru(3)–C(32)	161.7 (4)	Ru(1)–Ru(3)–C(33)	101.2 (4)	Ru(2)–C(1)–Ru(3)	79.4 (3)	Ru(2)–C(1)–C(2)	71.3 (6)
Ru(2)–Ru(3)–C(1)	52.7 (3)	Ru(2)–Ru(3)–C(31)	92.2 (4)	Ru(3)–C(1)–C(2)	137.5 (7)	Ru(1)–C(2)–Ru(2)	79.4 (3)
Ru(2)–Ru(3)–C(32)	102.1 (4)	Ru(2)–Ru(3)–C(33)	160.3 (4)	Ru(1)–C(2)–C(1)	81.2 (6)	Ru(1)–C(2)–C(3)	132.7 (7)
C(1)–Ru(3)–C(31)	136.1 (5)	C(1)–Ru(3)–C(32)	119.5 (5)	Ru(2)–C(2)–C(1)	74.5 (6)	Ru(2)–C(2)–C(3)	133.2 (8)
C(1)–Ru(3)–C(33)	112.6 (5)	C(31)–Ru(3)–C(32)	90.1 (6)	C(1)–C(2)–C(3)	133.4 (9)	Pt–C(4)–Ru(4)	82.7 (4
C(31)–Ru(3)–C(33)	92.9 (6)	C(32)–Ru(3)–C(33)	96.9 (5)	Pt–C(4)–Ru(5)	126.7 (5)	Pt–C(4)–Ru(6)	148.7 (5)
Pt–Ru(4)–Ru(5)	88.1 (1)	Pt–Ru(4)–Ru(6)	98.8 (1)	Pt–C(4)–C(5)	138.6 (8)	Ru(4)–C(4)–Ru(5)	80.4 (3)
Pt–Ru(4)–C(4)	47.6 (3)	Pt–Ru(4)–C(41)	171.6 (4)	Ru(4)–C(4)–Ru(6)	79.2 (4)	Ru(4)–C(4)–C(5)	138.4 (7)
Pt–Ru(4)–C(42)	80.3 (4)	Pt–Ru(4)–C(43)	90.2 (4)	Ru(5)–C(4)–Ru(6)	75.0 (3)	Ru(5)–C(4)–C(5)	69.9 (6)
Ru(5)–Ru(5)–Ru(6)	60.0 (1)	Ru(5)–Ru(4)–C(4)	53.0 (3)	Ru(6)–C(4)–C(5)	65.6 (6)	Ru(5)–C(5)–Ru(6)	79.7 (4)
Ru(5)–Ru(4)–C(41)	92.0 (4)	Ru(5)–Ru(4)–C(42)	102.7 (4)	Ru(5)–C(5)–C(4)	74.6 (6)	Ru(5)–C(5)–C(6)	134.8 (7)
Ru(5)–Ru(4)–C(43)	160.8 (4)	Ru(6)–Ru(4)–C(4)	54.7 (3)	Ru(6)–C(5)–C(4)	79.4 (6)	Ru(6)–C(5)–C(6)	133.0 (7)
Ru(6)–Ru(4)–C(41)	88.4 (4)	Ru(6)–Ru(4)–C(42)	162.6 (4)	C(4)–C(5)–C(6)	132.4 (9)	Ru–C–O(carbonyl)	177.0 (10)[a]

[a] Mean value

clusters in which metal alkylidyne moieties are linked by Pt atoms, an archetypal example being the complex $Pt[(\eta\text{-}C_5H_5)(CO)_2W{\equiv}CC_6H_4Me\text{-}4]_2$.[19] All the compounds mentioned above contain semibridging carbonyl ligands that interact with the Pt centers, but complex **5** does not exhibit such behavior. All CO ligands in **5** are essentially linear (mean 177 (1)°, range 173 (1)–179 (1)°), and the shortest Pt···C contact [Pt···C(42)] is 3.01 (1) Å.

The C_α–C_β distances in **5** (1.322 (13) and 1.367 (14) Å) compare with the corresponding value of 1.332 (8) Å found in complexes **1** and **3**.[1] These values are all longer than found in the parent Ru_3 cluster **2** (C_α–C_β = 1.312 (3) Å[2a]), though the differences are not at a statistically significant level. Taken together with the more acute substituent bend-back angles at C_β found in complexes **5** [133.4 (9) and 132.4 (9)°], **1** [131.1 (5)°],[1] and **3** [135.2 (6)°][1] as compared with **2** [141.0 (2)°],[2a] the structural data are consistent with a greater sp^2 character for the alkynyl moiety in the μ_4 clusters.

Fluxional Behavior of Complex 5. Complex **5**, possessing a C_2 axis as the sole molecular symmetry element, belongs to the point group C_2 and hence is necessarily chiral. Barring accidental degeneracies nine equally intense CO resonances are expected in the ^{13}C NMR spectrum, from the nine pairs of chemically distinct carbonyls. At the lowest temperature measured, 233 K, six equally intense signals at δ 195.2, 194.7, 189.5, 189.1, 188.1, and

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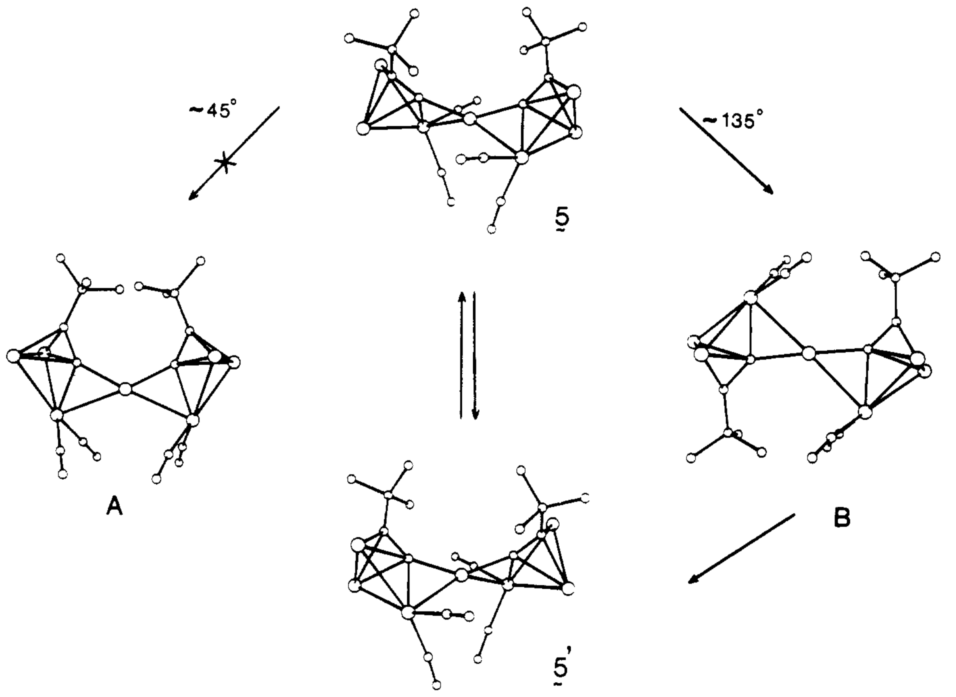
(17) (a) Elliot, G. P.; Howard, J. A. K.; Mise, T.; Moore, I.; Nunn, C. M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1986**, 2091. (b) Davies, S. J.; Elliot, G. P.; Howard, J. A. K.; Nunn, C. M.; Stone, F. G. A. *Ibid.* **1987**, 2177. (c) Elliot, G. P.; Howard, J. A. K.; Mise, T.; Nunn, C. M.; Stone, F. G. A. *Ibid.* **1987**, 2189.

(18) Elliot, G. P.; Howard, J. A. K.; Mise, T.; Nunn, C. M.; Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1986**, *26*, 190.

(19) Ashworth, T. V.; Chetcuti, M. J.; Howard, J. A. K.; Stone, F. G. A.; Wisbey, S. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1981**, 763.

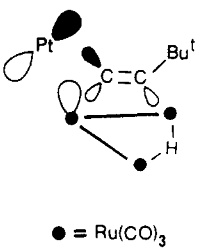
Scheme I



187.8 and a broad resonance at ca. δ 194 are observed (Figure 2). The broad signal is attributed to the six carbonyls on Ru(3) and Ru(4) that are undergoing a rapid tripodal rotation. This resonance sharpens on warming to give, at 338 K, a narrow signal with ^{195}Pt satellites (δ 193.9, $J(^{195}\mathrm{Pt{-}C}) = 31$ Hz). The other six signals, due to the carbonyls on the remaining Ru atoms, collapse in a pairwise fashion on warming to 298 K, giving three resonances δ 194.5, 189.1, and 187.9. This indicates that each $\mathrm{Ru_3}$ subunit, and the molecule as a whole, is acquiring a time-averaged mirror plane; i.e., the cluster is racemizing. Selective ^{1}H-decoupling experiments at 298 K are consistent with these assignments and the interpretation of the variable-temperature behavior. Thus the signal at δ 187.9 shows a coupling of 13 Hz to the hydride, indicating that it is due to the four carbonyl carbons [C(13), C(22), C(51), and C(62)] trans to the hydride. The signal at δ 189.1 shows a much smaller coupling of 3 Hz to the hydride, while that at δ 194.5 shows only a slight line broadening in the ^{1}H-coupled spectra, consistent with CO's which are cis with respect to the hydride. The sharp signal at δ 194.3 shows, as expected, no detectable coupling to the hydride. Above 298 K a further fluxional process is evident, since the resonances at δ 194.5, 189.1, and 187.9 broaden. This is attributed to a tripodal rotation in the (now equivalent) $\mathrm{Ru(CO)_3}$ groups on Ru(1), Ru(2), Ru(5), and Ru(6).

From the coalescence temperature of 266 (±5) K for the resonances at δ 189.5 and 189.1 ($\Delta\nu = 15.5 \pm 1.0$ Hz), an estimate for $\Delta G^{\ddagger}_{266}$ of 57.1 (±1.1) kJ mol^{-1} is obtained for the barrier to racemization. The interconversion of enantiomers, **5** ⟺ **5′** (Scheme I), requires an achiral transition state or intermediate, and this is most obviously achieved by rotation of one subunit about the Pt–MPT (or Pt–Ru) axis, giving the pseudo-square-planar configuration A or B. Configuration A is unlikely in view of the unacceptably close contacts between the two *t*-Bu groups. A restricted rotation by about 135° gives the alternative planar configuration B, where steric interactions are less severe. A chiral transoid isomer of **5**, resulting from a small twist in the configuration B, may be present in solution, but due to the very poor solubility of **5** at low temperatures, high-quality ^{13}C NMR spectra could not be obtained to confirm this possibility.

Chart I



Rosenberg and co-workers[20] have recently proposed, from variable-temperature ^{13}C NMR studies, that the related skeletally chiral Hg-bridged cluster $\mathrm{Hg[Ru_3\{\mu_3\text{-}\eta^2\text{-}C{\equiv}C(\mathit{t}\text{-}Bu)\}(CO)_9]_2}$ (**6**) exists as a mixture of cisoid and transoid isomers in solution. The NMR evidence for racemization of **6** is ambiguous, though phosphine-substituted analogues apparently show racemization.[20] Moreover, we have previously shown[14d] that the clusters $\mathrm{Hg[Fe_2M(\mu_3\text{-}COMe)(CO)_7(\eta\text{-}C_5H_5)]_2}$, with a similar chiral C_2 metal core, undergo rapid enantiomerization at 213 K for M = Co and more complex fluxional behavior involving Hg migration for M = Rh.[21] Intermediates with μ_3-Hg geometries have been proposed by Rosenberg[20] for the fluxional processes in **6** and related clusters, though a similar μ_3-Pt intermediate in complex **5** in much less likely.

The nature of the bonding of the Pt atom to the cluster subunits in **5** is not immediately obvious. The diamagnetism and the pseudotetrahedral ground-state geometry strongly imply a d^{10} rather than a d^8 configuration for the Pt atom.[22] With an sp^2 formalism (Chart I) for the alkynyl

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[20] Hajela, S.; Novak, B. M.; Rosenberg, E. *Organometallics* **1989**, *8*, 468.

[21] It should be noted that in these Hg-bridged systems the Hg–M connectivities differ from those of the Pt atom in **5**, since the Hg atom is effectively replacing two hydride ligands. The electronic contribution to the rotation barrier about the Hg atom is likely to be very small, and steric factors probably provide the major component.

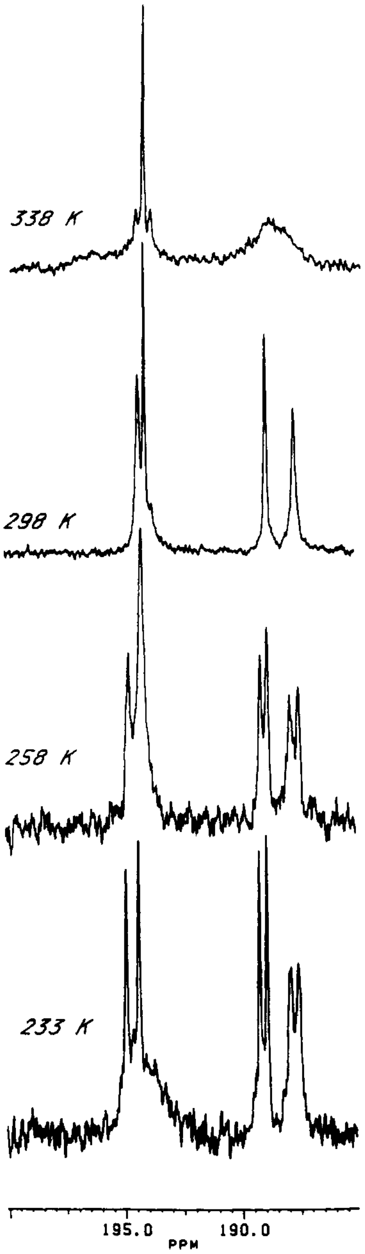

Figure 2. Variable-temperature $^{13}C\{^1H\}$ NMR spectrum of complex **5** in the carbonyl region.

ligand, it is possible to envisage a π-component to the Pt–(Ru–C_α) bond, so that **5** may be viewed as an analogue of $Pt(alkene)_2$.[24] Alternatively, the bonding may more closely resemble that in pseudolinear phosphine complexes, e.g. $Pt(PCy_3)_2$.[27] Although an MO study on $Ru_3(\mu$-H)(μ_3-η^2-C≡CMe)$(CO)_9$ has been reported,[28] this work focussed on the bonding of the alkynyl ligand to the cluster, and no details of possible donor and acceptor orbitals associated with the Ru–C_α vector were given. Clearly a detailed MO analysis is required to elucidate the bonding in **5**.

As a final point, it is interesting to note that at the highest temperature measured (338 K) there is no evidence for inter-Ru CO scrambling in **5**. Previous studies have shown that apparent inter-Ru CO scrambling is a low-energy process in the clusters **2**[29] and [Ru_3{μ_3-η^2-C≡C(t-Bu)}$(CO)_9]^-$[30] but not in phosphine-substituted derivatives.[3,31] These observation are consistent with a rotation of the alkynyl moiety about the Ru_3 triangle being the cause of apparent inter-Ru CO scrambling rather than actual motion of the carbonyls. Such alkynyl rotation has been previously proposed[3,32] and recently observed.[31c] The occurrence of such a process in **5**, as a *degenerate* mechanism, would require not only rotation of the alkynyl moiety and migration of the hydride ligand but also migration of the Pt atom to another Ru vertex. There is no evidence for such a process in **5**, though Hg migration has been proposed[20] as a possible high-energy fluxional process in the related Hg-bridged cluster **6**.

Experimental Section

All manipulations were carried out under dry, oxygen-free dinitrogen atmosphere, using standard vacuum line/Schlenk tube techniques. Solvents were deoxygenated and freshly distilled under dinitrogen prior to use; petroleum ether refers to that fraction with a boiling point of 40–60 °C. NMR spectra were obtained on a Bruker WP200 or AM200 FT NMR spectrometer. Chemical shifts were referenced to internal solvent signals and are reported relative to Me_4Si. Infrared spectra were measured on a Perkin-Elmer 983 photospectrometer. Elemental analyses (C/H) were performed by the Microanalytical Unit in the Department of Chemistry, University of Glasgow. $Pt(COD)_2$, $Ru_3Pt(\mu$-H){μ_4-η^2-C≡C(t-Bu)}$(CO)_9$(COD), and $Ru_3(\mu$-H){μ_3-η^2-C≡C(t-Bu)}$(CO)_9$ were prepared by literature methods,[1,2b,7b] and the latter was enriched with ^{13}CO by heating a sample at 90 °C for 2 days under 1 atm of ^{13}CO (99% ^{13}C).

Preparation of Pt[$Ru_3(\mu$-H){μ_4-η^2-C≡C(t-Bu)}$(CO)_9]_2$ (5). Method 1. A sample of $Ru_3Pt(\mu$-H){μ_4-η^2-C≡C(t-Bu)}$(CO)_9$(COD) (0.1 g, 0.11 mmol) in dichloromethane or toluene (5 mL) was left at ambient temperature for 5 days. The solution darkened considerably, and orange crystals were deposited. These crystals were washed with petroleum ether (2 × 5 mL) affording bright orange, analytically pure **5** (0.04 g, 50% yield).

Method 2. A solution of $Ru_3(\mu$-H){(μ_3-η^2-C≡C(t-Bu)}$(CO)_9$ (0.1 g, 0.15 mmol) in diethyl ether (20 mL) was added slowly to a solution of $Pt(C_2H_4)_3$ in diethyl ether at 0 °C [prepared in situ by adding $Pt(COD)_2$ (0.031 g, 0.075 mmol) to diethyl ether (20 mL) saturated with ethylene]. The solution turned orange and then brown on warming to room temperature for 15 min. The volatiles were removed, and the residue was dissolved in the minimum dichloromethane and passed down a short column of Florosil. The orange eluate was collected, and concentration and cooling overnight at −20 °C afforded orange crystals of **5** (0.048 g, 44% yield). A ^{13}CO-enriched sample of **5** was prepared by this method: IR (CH_2Cl_2) ν_{max}(CO) 2098 (vw), 2086 (m), 2072 (s), 2046 (m), 2018 (m, br), 1982 (w, br) cm^{-1}; ^1H NMR ($CDCl_3$, 298 K) δ

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[22] There are no well authenticated examples of Pt(II) complexes with ground-state tetrahedral geometries. In d^8 complexes the thermal tetrahedral ⇔ square-planar interconversion is orbitally forbidden (see ref 23).

[23] (a) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058. (b) Pearson, R. G. *Symmetry Rules for Chemical Reactions*; Wiley-Interscience: New York, 1976. (c) Whitesides, T. H. *J. Am. Chem. Soc.* **1969**, *91*, 2395.

[24] Although no stable $Pt(alkene)_2$ complexes are known, several examples of $Pt(alkyne)_2$ compounds have been reported.[25] Theoretical calculations on the hypothetical molecule $Ni(C_2H_4)_2$ indicate[26] that the pseudotetrahedral D_{2d} structure is preferred over the planar D_{2h} configuration by ca. 6 kJ mol^{-1}. Barriers to alkyne rotation in the $Pt(alkyne)_2$ compounds are probably higher,[25] but not excessive.

[25] Boag, N. M.; Howard, J. A. K.; Green, M.; Grove, D. M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 2170.

[26] Rösch, N.; Hoffmann, R. *Inorg. Chem.* **1974**, *13*, 2656.

[27] Immirzi, A.; Musco, A.; Zambelli, P.; Garturan, G. *Inorg. Chim. Acta* **1975**, *13*, L13.

[28] Granozzi, G.; Tondello, E.; Bertoncello, R.; Aime, S.; Osella, D. *Inorg. Chem.* **1983**, *22*, 744.

[29] Rosenberg, E.; Milone, L.; Aime, S. *Inorg. Chim. Acta* **1975**, *15*, 53.

[30] Barner-Thorsen, Hardcastle, K. I.; Rosenberg, E.; Siegel, J.; Manotti Landfredi, A. M.; Tiripicchio, A.; Tiripicchio Camellini, M. *Inorg. Chem.* **1981**, *20*, 4306.

[31] (a) Rosenberg, E.; Barner Thorsen, C.; Milone, L.; Aime, S. *Inorg. Chem.* **1985**, *24*, 231. (b) Predieri, G.; Tiripicchio, A.; Vignali, C.; Sappa, E. *J. Organomet. Chem.* **1988**, *342*, C33.

[32] Rosenberg, E.; Wang, J.; Gellert, R. W. *Organometallics* **1988**, *7*, 1093.

Table III. Experimental Data for Crystallographic Study

formula	$C_{30}H_{20}O_{18}PtRu_6$
M_r	1470.0
space group	$P\bar{1}$ (No. 2, C_i^1)
cryst system	triclinic
a/Å	9.546 (2)
b/Å	12.993 (2)
c/Å	17.786 (2)
α/deg	72.97 (1)
β/deg	82.48 (1)
γ/deg	74.62 (2)
V/Å^3	2030.4 (6)
Z	2
D_{calcd}/g cm^{-3}	2.40
$F(000)$	1372
μ(Mo Kα)/cm^{-1}	56.7
T/K	298
scan mode	$\theta/2\theta$
θ range/deg	$2 < \theta < 25$
cryst size/mm	0.05 × 0.05 × 0.50
range of trans coeff corr	0.817/1.132
no. of data collected	7612
no. of unique data	7145
std reflctns	$\bar{2}\bar{6}\bar{2}$, $\bar{2}5\bar{2}$
observability criterion ($I > n\sigma(I)$), n	3.0
no. of data in refinement	4806
no. of refined parameters	280/280
final R	0.033
R_w	0.038
largest remaining feature in elec density map, e Å^{-3}	+1.07 (max), −0.89 (min)
shift/esd in last cycle	0.03 (max), 0.005 (av)

1.47 (s, 18 H, *t*-Bu), −20.71 (s, 2 H, Ru(μ-H)Ru, *J*(Pt–H) = 14 Hz); ^{13}C NMR (CD_2Cl_2, 298 K) δ 194.6 (s, 4 C, CO), 194.3 (s, 6 C, CO, *J*(Pt–C) = 31 Hz), 189.1 (s, 4 C, CO), 187.9 (s, 4 C, CO), 40.0 (s, 2 C, *C*$(CH_3)_3$), 35.2 (s, 6 C, C$(CH_3)_3$). For CO shifts at other temperatures, see text. Anal. Calcd for $C_{30}H_{20}O_{18}PtRu_6$: C, 24.51; H, 1.37. Found: C, 24.59; H, 1.52.

Crystal Structure Determination. Details of data collection procedures and structure refinement are given in Table III. Data were collected on an Enraf-Nonius CAD4F automated diffractometer, with graphite-monochromated X-radiation (λ = 0.71069 Å). Unit cell parameters were determined by refinement of the setting angles ($\theta \geq 12°$) of 25 reflections. Standard reflections were measured every 2 h during data collection, and a decay corresponding to 2.5% over 10000 data was observed and corrected for. Lorentz–polarization and absorption (DIFABS[33]) corrections were also applied. Laue symmetry and normalized structure factor statistics indicated the centrosymmetric space group $P\bar{1}$. The structure was solved by direct methods (MITHRIL[34]) and subsequent electron density difference syntheses. All non-hydrogen atoms were allowed anisotropic thermal motion. Hydride positions were determined from potential energy minimization calculations (XHYDEX,[35] Ru–H = ca. 1.75 Å) and are consistent with the NMR data insofar as they are in chemically equivalent positions bridging Ru–Ru vectors. Methyl hydrogens were included at calculated positions with C–H = 1.0 Å. Isotropic thermal parameters for H atoms were fixed at 0.05 Å^2. Refinement was by full-matrix least squares, but due to matrix size limitations the parameters were divided into two blocks of 280 and each refined separately. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with the weighting scheme $w = [\sigma^2(F_o)]^{-1}$ used and judged satisfactory. $\sigma(F_o)$ was estimated from counting statistics. Neutral atom scattering factors were taken from ref 36 with corrections for anomalous dispersion. All calculations were carried out on a Gould-SEL 32/27 minicomputer using the GX suite of programs.[37]

Acknowledgment. Johnson Matthey is thanked for a generous loan of Pt and Ru salts.

Registry No. 1, 119593-13-4; **2**, 57673-31-1; **5**, 123857-98-7; Pt(COD)$_2$, 12130-66-4; ethylene, 74-85-1; platinum, 7440-06-4; ruthenium, 7440-18-8.

Supplementary Material Available: Tables of anisotropic thermal parameters and calculated hydrogen positional parameters and complete listings of bond lengths and angles (9 pages); listings of calculated and observed structure factors (23 pages). Ordering information is given on any current masthead page.

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(33) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.

(34) Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42.

(35) Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509.

(36) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, 1974; Vol 4.

(37) Mallinson, P.; Muir, K. W. *J. Appl. Crystallogr.* **1985**, *18*, 51.