spectra of **2c'** are identical to those of **2c** with the exception of the signal for the carbon atom of the anion $CF_3SO_2^-$ at $\delta = 120.7$ (q, $J = 320$ Hz).

2d: ^{1}H NMR (200 MHz, CD_2Cl_2, TMS): $\delta = 7.95$ (m, 4H), 7.56 (m, 3H), 5.43 (d, 1H, $^2J = 12$ Hz), 4.90 (d, 1H, $^2J = 12$), 4.77 (AB system, $^2J = 13$ Hz, $\Delta\nu = 15$ Hz), 3.79 (td, 1H, $^3J = 10.5$, 10.5, 4.5 Hz), 2.10 (m, 1H), 1.90 (m, 2H), 1.76 (s, 3H), 1.74 (s, 3H), 1.6 (m, 2H), 1.4 (q, 1H, $J = 11$ Hz), 1.1 (m, 2H), 1.0 (d, 3H, $^3J = 6.5$ Hz); ^{13}C NMR (50 MHz, $CDCl_3$, TMS): $\delta = 134.1$, 133.8, 124.1, 71.5 (C), 131.4, 130.6, 128.5, 128.3, 128.2, 127.7, 127.0, 78.7, 43.7, 31.4 (CH), 58.5, 40.4, 36.9, 34.3, 24.1 (CH_2), 26.2, 22.0, 21.1 (CH_3).

4a: ^{1}H NMR (200 MHz, $CDCl_3$, TMS): $\delta = 7.27$ (m, 3H), 7.13 (m, 2H), 4.18 (q, 2H, $^3J = 7$), 2.53 (ddd, 1H, $J = 9.5$, 6.5, 4 Hz), 1.91 (ddd, 1H, $J = 8.5$, 5.5, 4.5 Hz), 1.61 (ddd, 1H, $J = 9.5$, 5.5, 4.5 Hz), 1.32 (ddd, 1H, $J = 8.5$, 6.5, 4.5 Hz), 1.29 (t, 3H, $^3J = 7$ Hz); ^{13}C NMR (50 MHz, $CDCl_3$, TMS): $\delta =$ 173.5, 140.2 (C), 128.5, 126.5, 126.2, 26.3, 24.2, (CH), 60.7, 17.1 (CH_2), 14.4 (CH_3).

4b: ^{1}H NMR (200 MHz, $CDCl_3$, TMS): $\delta = 7.50$ (d, 2H, $^3J = 8$ Hz), 7.13 (d, 2H, $^3J = 8$ Hz), 4.15 (q, 2H, $^3J = 7$ Hz), 2.49 (ddd, 1H, $J = 10$, 6.5, 4 Hz), 1.91 (ddd, 1H, $J = 8.5$, 5.5, 4 Hz), 1.62 (ddd, 1H, $J = 10$, 5.5, 4.5 Hz), 1.29 (ddd, 1H, $J = 8.5$, 6.5, 4.5 Hz), 1.22 (t, 3H, $^3J = 7$ Hz).

4c: ^{1}H NMR (200 MHz, $CDCl_3$, TMS): $\delta = 7.33$ (d, 2H, $^3J = 8.5$ Hz), 7.06 (d, 2H, $^3J = 8.5$ Hz), 4.16 (q, 2H, $^3J = 7$ Hz), 2.51 (ddd, 1H, $J = 9.5$, 6.5, 4 Hz), 1.90 (ddd, 1H, $J = 8.5$, 5, 4 Hz), 1.60 (ddd, 1H, $J = 9.5$, 5, 4 Hz), 1.34 (ddd, 1H, $J = 8.5$, 6.5, 4 Hz), 1.32 (s, 9H), 1.29 (t, 3H, $^3J = 7$ Hz).

4d: ^{1}H NMR (200 MHz, $CDCl_3$, TMS): $\delta = 7.78$ (m, 3H), 7.57 (s, 1H), 7.45 (m, 2H), 7.21 (dd, 1H, $^3J = 8.5$, $^4J = 2$ Hz), 4.19 (q, 2H, $^3J = 7$ Hz), 2.69 (ddd, 1H, $J = 9.5$, 6.5, 4.5 Hz), 2.01 (ddd, 1H, $J = 8.5$, 5, 4.5 Hz), 1.67 (ddd, 1H, $J = 9.5$, 5, 4.5 Hz), 1.47 (ddd, 1H, $J = 8.5$, 6.5, 4.5 Hz), 1.30 (t, 3H, $^3J =$ 7 Hz); ^{13}C NMR (50 MHz, $CDCl_3$, TMS): $\delta = 173.5$, 137.6, 133.5, 132.4 (C), 128.3, 127.7, 127.5, 126.4, 125.6, 124.9, 124.6, 26.5, 24.3 (CH), 60.9, 17.2 (CH_2), 14.4 (CH_3).

6: ^{1}H NMR (200 MHz, $CDCl_3$, TMS): $\delta = 7.30$ (m, 3H), 7.10 (m, 2H), 2.53 (ddd, 1H, $J = 9$, 6.5, 4 Hz), 2.32 (s, 3H), 2.23 (ddd, 1H, $J = 8$, 5, 4 Hz), 1.70 (ddd, 1H, $J = 9$, 5, 4 Hz), 1.39 (ddd, 1H, $J = 8$, 6.5, 4 Hz); ^{13}C NMR (50 MHz, $CDCl_3$, TMS): $\delta = 207.0$, 140.4 (C), 127.5, 126.5, 126.1, 33.0, 30.9, 29.1 (CH, CH_3), 19.2 (CH_2).

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[1] A. Solladié-Cavallo, A. Diep-Vohuule, V. Sunjic, V. Vinkovic, *Tetrahedron: Asymmetry* **1996**, *7*, 1783.

[2] H. E. Simmons, R. D. Smith, *J. Am. Chem. Soc.* **1958**, *80*, 5323.

[3] A. B. Charette, S. Prescott, C. Brochu, *J. Org. Chem.* **1995**, *60*, 1081.

[4] A. B. Charette, C. Brochu, *J. Am. Chem. Soc.* **1995**, *117*, 11367.

[5] D. A. Evans, K. A. Woerpel, M. M. Hinman, M. M. Faul, *J. Am. Chem. Soc.* **1991**, *113*, 726.

[6] S. E. Denmark, S. P. O'Connor, *J. Org. Chem.* **1997**, 62, 584.

[7] H. Fritschi, U. Leutenegger, A. Pfaltz, *Helv. Chim. Acta* **1988**, *71*, 1553.

[8] E. J. Corey, M. Jautelat, *J. Am. Chem. Soc.* **1967**, *89*, 3912.

[9] M. Calmes, J. Daunis, F. Escale, *Tetrahedron: Asymmetry* **1996**, *7*, 395.

[10] M. J. De Vos, A. Krief, *Tetrahedron Lett.* **1983**, *24*, 103.

[11] a) E. Vedejs, D. A. Engler, *Tetrahedron Lett.* **1976**, 3487; b) E. Vedejs, D. A. Engler, M. J. Mullins, *J. Org. Chem.* **1977**, *42*, 3109.

[12] A. Solladié-Cavallo, A. Adib, M. Schmitt, J. Fischer, A. DeCian; *Tetrahedron: Asymmetry* **1992**, *3*, 1597.

[13] Such phosphazene bases provide very reactive naked anions. One could expect the large $Et-P_2H^+$ cation to be less tightly associated to its anion and to the ylide, thus allowing an easy access to the ylide. Furthermore, it should be geometrically able to help form the complex of the ylide and the Michael substrate in the transition state.

[14] R. Schwesinger, H. Schlemper, *Angew. Chem.* **1987**, 99, 1212; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1167.

[15] In all cases the CH_2 protons of the ester groups are more shielded (due to the phenyl effect) in the *cis* isomer ($\delta \approx 3.85$, $CDCl_3$) than in the *trans* isomer ($\delta \approx 4.20$, $CDCl_3$). This was already observed for the aldehydic proton in formylphenylcyclopropane: P. Scribe, J. Wiedmann, *Bull. Soc. Chim. Fr.* **1971**, 2268.

[16] The enantiomeric purities were determined by Dr. V. Vinkovic in the group of Prof. V. Sunjic at the Ruder Boskovic Institut of Zagreb.

[17] Y. Inouye, T. Sugita, H. M. Walborsky, *Tetrahedron* **1964**, *20*, 1695.

[18] D. A. Evans, K. A. Woerpel, M. J. Scott, *Angew. Chem.* **1992**, 104, 439; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 430.

Multiple Coordination of Metal Atoms to Arenes: The Coordination of Six Ruthenium Atoms to Naphthalene-1,8-diyl in $[Ru_6(\mu_6\text{-}C_{10}H_6)(\mu_3\text{-PPh})(CO)_{14}]$**

Antony J. Deeming* and Caroline M. Martin

Research on the incorporation of arenes into clusters has largely been stimulated by their potential as models for chemisorption on metal surfaces and by a wish to modify arene structure and reactivity.[1, 2] The chemistry of benzene with metal clusters has been developed extensively in recent years,[3] and dominant modes of coordination are η^6 coordination at a single metal atom, μ_3-η^2,η^2,η^2 coordination over a triangular cluster face, and combinations of these two modes with σ-M–C bonding, as observed in phenyl and *ortho*-phenylene (1,2-didehydrobenzene) systems. Several of these modes resemble chemisorption of benzene on a (111) metal surface or on step-sites on such surfaces.[4] In contrast, however, relatively few clusters that contain more complex, polycyclic arenes such as naphthalene and anthracene have been reported. Studies of such compounds are often hindered by the difficulty of introducing the polycyclic arene into the coordination sphere of the cluster, and has, so far, centered on mono- and binuclear species, with interactions through either σ bonds, as in $[Fe(C_{10}H_7)_4][LiOEt_2]_2$,[5] or more commonly by π complexation through η^2, η^4, η^6, or bis-allylic η^3:η^3 interactions, as in, for example, the compounds $[Rh_2(C_5Me_5)_2(1,2\text{-}\eta^2\text{-}3,4\text{-}\eta^2\text{-}C_{10}H_8)(PMe_3)_2]$,[6] $[RhCp(\eta^4\text{-}C_{14}H_{10})]$,[7] $[Ru(\eta^4\text{-}C_8H_{12})(\eta^6\text{-}C_{10}H_8)]$,[8] and $[Fe_2(CO)_6(\mu\text{-}\eta^3\text{:}\eta^3\text{-}C_{14}H_{10})]$.[9] One of our recent objectives has therefore been to extend the coordination chemistry of naphthalene and anthracene by the combination of the σ and π M–C interactions that are present in the above molecules, to allow extensive metalation of each ring of the polycyclic arene.

We have introduced polycyclic arenes into the clusters by the thermal degradation of tertiary phosphanes in the presence of metal compounds. The thermolysis of $[Ru_3(CO)_{12}]$

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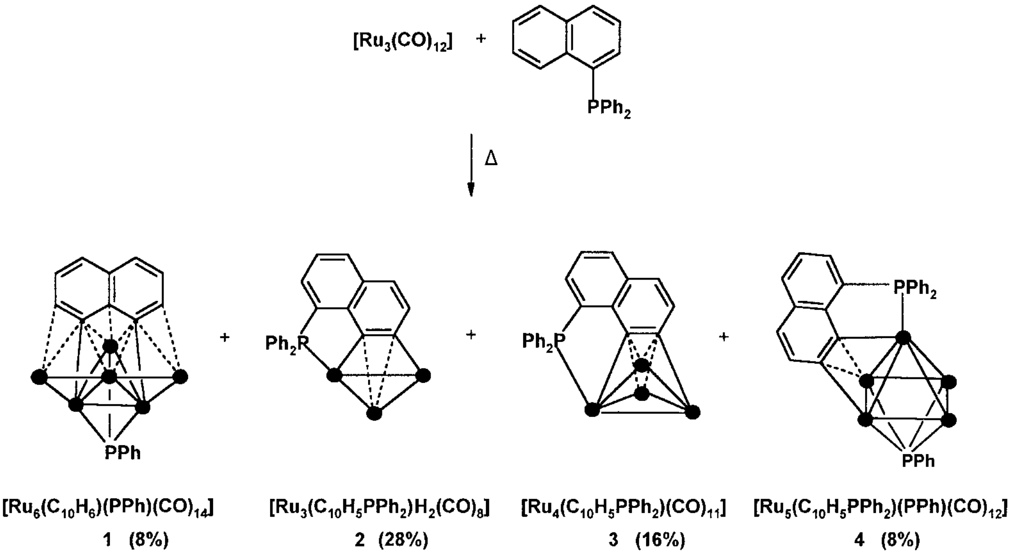
with (1-naphthyl)diphenylphosphane yields a number of cluster derivatives (**1**–**4**), which generally retain the original P–C(naphthyl) bond (Scheme 1). The crystal structures of compounds $[Ru_3(C_{10}H_5PPh_2)H_2(CO)_8]$ (**2**), $[Ru_4(C_{10}H_5PPh_2)(CO)_{11}]$ (**3**), and $[Ru_5(C_{10}H_5PPh_2)(PPh)(CO)_{12}]$ (**4**) will be reported elsewhere.[10] Here we present the title compound $[Ru_6(\mu_6\text{-}C_{10}H_6)(\mu_3\text{-}PPh)(CO)_{14}]$ (**1**), which contains a naphthalene-1,8-diyl moiety. This was formed by C–H cleavage at the 8-position together with P–C(naphthyl) bond activation. Complex **1** is unique in that the naphthalene-1,8-diyl group interacts through five carbon atoms to all six metal centers in the cluster framework in a rather dramatic manner; in addition to two Ru–C σ bonds at the 1 and 8 positions, there are also two η^3 and two η^2 interactions.

Compound **1** was initially identified on the basis of IR and NMR spectroscopy, and mass spectrometry;[10] the mass spectrum exhibits a parent ion at *m/z* 1233 (most abundant isotopomer; calculated: *m/z* 1233), and the ^1H NMR spectrum shows a well-resolved ABC pattern, indicative of a symmetrically 1,8-disubstituted naphthalene group, together with a multiplet attributable to the phenyl protons. The molecular structure of **1** was confirmed by a single-crystal X-ray structure analysis and is shown in Figure 1.[11]

Complex **1** has a triangular "raftlike" cluster geometry[12] in which five of the ruthenium atoms are approximately coplanar and the sixth, Ru(1), is out of this plane by 2.367 Å. Hence, the Ru(1)-Ru(2)-Ru(3) triangular face, which is asymmetrically capped by a phosphanidene ligand, is tilted away from the Ru_5 plane with a dihedral angle of 105°. The C_{10} plane of the naphthalene lies at an angle of 42.0 and 63.1° to the Ru_5 and Ru_3 planes, respectively, which enables interaction with all six metal atoms. There are two η^2 interations between C(1n)–C(2n) and Ru(4), and C(8n)–C(9n) and Ru(6), while the C(1n)-C(10n)-C(9n) unit interacts in an η^3-allylic manner with both Ru(1) and Ru(5), and there are two σ bonds C(1n)–Ru(2) and C(9n)–Ru(3). Figure 2 shows three views of the Ru_6C_{10} core. Fourteen terminal carbonyl ligands complete the coordination sphere of the cluster.



Scheme 1. Thermolysis of $[Ru_3(CO)_{12}]$ and (1-naphthyl)diphenylphosphane.

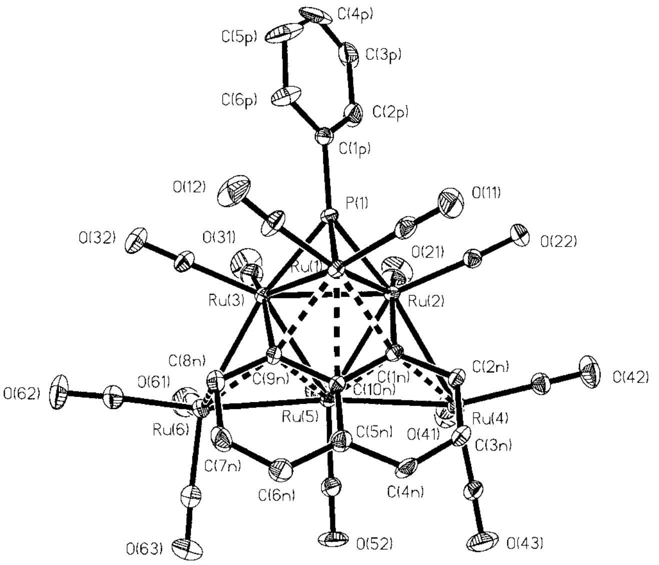


Figure 1. Molecular structure of **1**; the C atoms of the CO groups bear the same numbers as the corresponding O atoms. Selected bond distances [Å] and dihedral angles [°]: Ru(1)–Ru(2) 2.835(1), Ru(1)–Ru(3) 2.815(1), Ru(2)–Ru(3) 2.807(1), Ru(2)–Ru(4) 2.808(1), Ru(2)–Ru(5) 2.702(1), Ru(3)–Ru(5) 2.701(1), Ru(3)–Ru(6) 2.799(1), Ru(4)–Ru(5) 2.772(1), Ru(5)–Ru(6) 2.783(1), Ru(1)–P(1) 2.221(2), Ru(2)–P(1) 2.253(2), Ru(3)–P(1) 2.271(2), Ru(1)–C(1n) 2.267(6), Ru(1)–C(9n) 2.274(7), Ru(1)–C(10n) 2.397(7), Ru(2)–C(1n) 2.154(7), Ru(3)–C(9n) 2.142(7), Ru(4)–C(1n) 2.486(6), Ru(4)–C(2n) 2.266(7), Ru(5)–C(1n) 2.465(7), Ru(5)–C(9n) 2.480(7), Ru(5)–C(10n) 2.310(7), Ru(6)–C(8n) 2.265(8), Ru(6)–C(9n) 2.461(9), C(1n)–C(2n) 1.440(9), C(1n)–C(10n) 1.440(10), C(2n)–C(3n) 1.425(10), C(3n)–C(4n) 1.338(12), C(4n)–C(5n) 1.424(11), C(5n)–C(6n) 1.421(13), C(5n)–C(10n) 1.454(10), C(6n)–C(7n) 1.345(14), C(7n)–C(8n) 1.431(12), C(8n)–C(9n) 1.439(11), C(9n)–C(10n) 1.470(10); Ru(2)Ru(3)Ru(5)-Ru(3)Ru(5)Ru(6) 6.9, Ru(2)Ru(3)Ru(5)-Ru(2)Ru(4)-Ru(5) 7.3, Ru(2)Ru(3)Ru(5)-Ru(1)Ru(2)Ru(3) 105.1, Ru(2)Ru(3)Ru(5)-P(1)Ru(2)Ru(3) 13.9, Ru(2)Ru(3)Ru(5)-C_{10}(naphth) 42.0, Ru(1)Ru(2)-Ru(3)-C_{10}(naphth) 63.1.

The naphthalene-1,8-diyl group in **1** is thought to donate eight electrons to the cluster framework: two through the σ bonds and six through extensive π interactions. The C–C bond lengths within the organic ring are in agreement with this proposition and suggest that C(3n)–C(4n) and C(6n)–C(7n) maintain their double bond character (mean 1.34(1) Å), whilst all other C–C bonds are lengthened (mean 1.44(1) Å). These eight electrons, together with those donated by the PPh and fourteen CO ligands, give a total valence-electron count of 88 for the cluster. This is two fewer, according to simple electron-counting rules, than required for an electron-precise cluster with nine M–M bonds.

Naphthalene is known to form four-membered met-

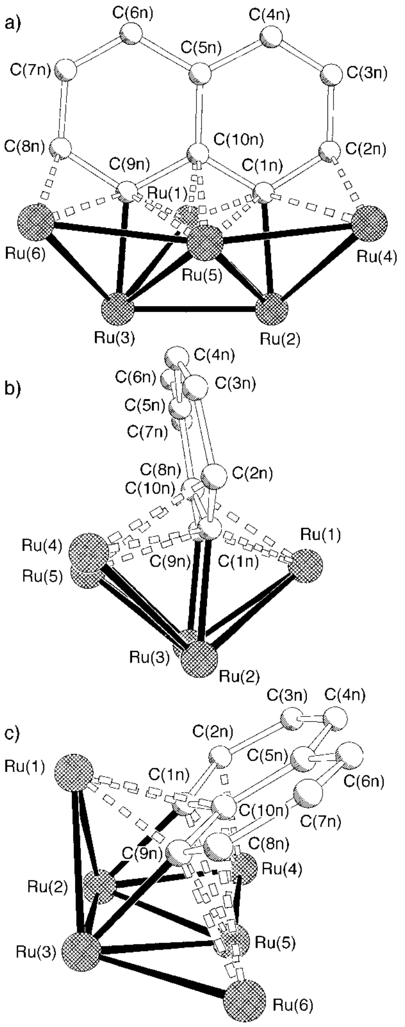


Figure 2. Three projections of the Ru_6C_{10} core of cluster **1**, showing the similarity to a step on a (111) Ru surface (a), the ten Ru–C bonding contacts (b), and the alignment of the C_{10} ligand within the metal cleft (c).

allacycles[13] with a single metal center, where it is coordinated in a 1,8-diyl fashion. It can also be coordinated as a 1,2-didehydronaphthalene unit as in the clusters $[Ru_4(\mu_4\text{-}C_{10}H_6)(\mu_4\text{-}AsC_{10}H_7)(CO)_{11}]$ and $[Ru_4(\mu_4\text{-}C_{10}H_6)(CO)_{12}]$.[14] However, as far as we are aware, this is the first time such extensive σ and π interactions have been observed between a polycyclic arene and a transition metal cluster. This illustrates, firstly, how it is possible to "load-up" such a simple organic molecule with metal atoms, which gives rise to the potential to construct clusters of higher nuclearity with the polycyclic arene as a convenient stable organic core about which an outer shell of metal atoms could be constructed. Secondly, our example shows how multiple coordination can stabilize an open geometric cluster framework. As the extent of σ and π bonding of the arene to the metal centers develops, one would predict increasing departure from normal arene behavior. Furthermore, one might envisage incorporation of another six Ru atoms on the opposite edge of the arene, to carbon atoms C(3n) to C(7n). In the context of the surface-cluster analogy, complex **1** might relate to the multiple interactions that could develop when naphthalene is chemisorbed at a step-site on a (111) metal surface.

Experimental Section

A solution of $[Ru_3(CO)_{12}]$ (0.100 g, 0.157 mmol) and $PPh_2(1\text{-}C_{10}H_7)$ (0.50 g, 1.60 mmol) in octane (30 mL) was heated to reflux for 4 h. The solvent was removed in vacuo and the mixture separated by thin-layer chromatography (SiO_2, CH_2Cl_2/hexane 3/7). Several products were isolated and characterized: $[Ru_3(\mu_3\text{-}C_{10}H_5PPh_2)(\mu\text{-}H)_2(CO)_8]$ (**2**) (yellow, 28%), $[Ru_4(\mu_4\text{-}C_{10}H_5PPh_2)(CO)_{11}]$ (**3**) (purple, 16%), and $[Ru_5(\mu_3\text{-}C_{10}H_5PPh_2)(\mu_4\text{-}PPh)(CO)_{12}]$ (**4**) (orange-brown, 8%), each of which contains a didehydronaphthalene group formed by double metalation at the 7,8-positions of the unsubstituted ring. The final product isolated was the title compound $[Ru_6(\mu_6\text{-}C_{10}H_6)(\mu_3\text{-}PPh)(CO)_{14}]$ (**1**) (purple-black, 8%).

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[1] a) B. F. G. Johnson, M. Gallup, Y. V. Roberts, *J. Mol. Catal.* **1994**, *86*, 51; b) B. F. G. Johnson, J. Lewis, M. Gallup, M. Martinelli, *Faraday Discuss. Chem. Soc.* **1991**, *92*, 241.

[2] E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Bruker, W. R. Pretzer, *Chem. Rev.* **1979**, *79*, 91.

[3] See for example: a) D. Braga, P. J. Dyson, F. Grepioni, B. F. G. Johnson, *Chem. Rev.* **1994**, *94*, 1585; b) B. F. G. Johnson, C. M. Martin, *J. Chem. Soc. Dalton Trans.* **1996**, 2395; c) J. P. H. Charmont, H. A. A. Dickson, N. J. Grist, J. H. Keister, S. A. R. Knox, D. A. V. Morton, A. G. Orpen, J. M. Viñas, *J. Chem. Soc. Chem. Commun*, **1991**, 1393.

[4] a) G. A. Somerjai, *J. Phys.Chem.* **1990**, *94*, 1013; b) M. A. Hove, R. F. Lin, G. A. Somerjai, *J. Am. Chem. Soc.* **1986**, *108*, 2532.

[5] T. A. Bazhenova, R. M. Labkovskaya, R. P. Shibaeva, A. K. Shilova, M. Gruselle, G. Leny, E. Deschamps, *J. Organomet. Chem.* **1983**, *244*, 375.

[6] R. M. Chin, L. Dong, S. B. Duckett, W. D. Jones, *Organometallics*, **1992**, *11*, 871.

[7] J. Müller, P. Escarpa Gaede, C. Hirsch, K. Qiao, *J.Organomet. Chem.* **1994**, *472*, 329.

[8] M. Crocker, M. Green, J. A. K. Howard, N. C. Norman, D. M. Thomas, *J. Chem. Soc. Dalton Trans.* **1990**, 2299.

[9] M. J. Begley, S. G. Puntambekar, A. H. Wright, *J. Chem. Soc. Chem. Commun.* **1987**, 1251.

[10] Spectroscopic data for **1**: IR (CH_2Cl_2): $\tilde{\nu} = 2077$ m, 2053 vs, 2029 s, 2018 s, 2004 m, 1974 cm^{-1} w (CO; ^1H NMR (400 MHz, $CDCl_2$): $\delta = 8.72$, (dd, $^3J = 8.28$, 5.96 Hz, 2H, $H^{3n,7n}$), 7.94 (m, 2H, *o*-Ph), 7.63 (m, 3H, *m*-, *p*-Ph), 7.16 (d, $^3J = 8.30$ Hz, 2H, $H^{4n,6n}$), 4.98 (d, $^3J = 5.92$ Hz, 2H, $H^{2n,8n}$); positive-ion FAB MS: calcd: 1233, found: 1233. Selected data for other products: **2**: $\tilde{\nu} = 2081$ s, 2049 s,br, 2038 m,sh, 2005 s,br, 1990 cm^{-1} m,sh (CO). **3**: $\tilde{\nu} = 2080$ m, 2058 vs, 2037 s,sh, 2025 s, 2010 s, 1952 cm^{-1} m,sh (CO). **4**: $\tilde{\nu} = 2078$ s, 2054 vs, 2042 vs, 2011 m,br, 1890 cm^{-1} m,sh (CO).

[11] X-ray crystal structure analysis of $[Ru_6(\mu_6\text{-}C_{10}H_6)(\mu_3\text{-}PPh)(CO)_{14}]$ **1**: black crystal from hexane, $C_{30}H_{11}O_{14}PRu_6$, $0.45 \times 0.40 \times 0.37$ mm^3, $M_r = 1232.80$, orthorhombic, space group $P2_12_12_1$, $a = 11.570(2)$, $b = 16.484(2)$, $c = 18.023(3)$ Å, $V = 3437.3(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.38$ g cm^{-3}, $\lambda(Mo) = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 135.6$ cm^{-1}, $F(000) = 2328$. Nicolet R3v/m diffractometer, direct methods (SHELXTL-PLUS), 4427 total data and 4399 unique data were collected (corrected for Lorentzian and polarization effects and for absorption by Ψ-scans, max./min. transmission factors, 0.966/0.765), $5 \leq 2\theta \leq 55°$. 4120 data with $I_o \geq 1.5\sigma(I_o)$ and 460 parameters (all non-hydrogen atoms anisotropic) were used in the refinement, final $R = 0.0286$ and $wR = 0.0310$ where $wR = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$ where $w = 1/[\sigma^2(F_o) + 0.000510 F_o^2]$. Hydrogen atoms added in calculated positions (C–H 0.96 Å) riding on the respective carbon atoms. Maximum peak in final difference Fourier $= 0.52$ e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100597. Copies of the data can be obtained free of charge on application to CCDC, 12

Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[12] See for example: a) R. J. Goudsmit, J. G. Jeffrey, B. F. G. Johnson, J. Lewis, R. S. C. McQueen, A. J. Sanders, J.-C. Liu, *J. Chem. Soc. Chem. Commun.* **1986**, 24; b) C. M. Hay, J. G. Jeffrey, B. F. G. Johnson, J. Lewis, P. R. Raithby, *J. Organomet. Chem.* **1989**, *359*, 87.

[13] M. G. M. Tinga, G. Schat, O. S. Akkerman, F. Bickelhaupt, W. J. J. Smeets, A. L. Spek, *Chem. Ber.* **1994**, *127*, 1851.

[14] W. R. Cullen, S. J. Rettig, T. C. Zheng, *Organometallics* **1995**, *14*, 1466.

Stepwise Assembly of $[(C_5H_5)_4(C_5Me_5)_4Co_4Rh_4(CN)_{12}]^{4+}$, an "Organometallic Box" **

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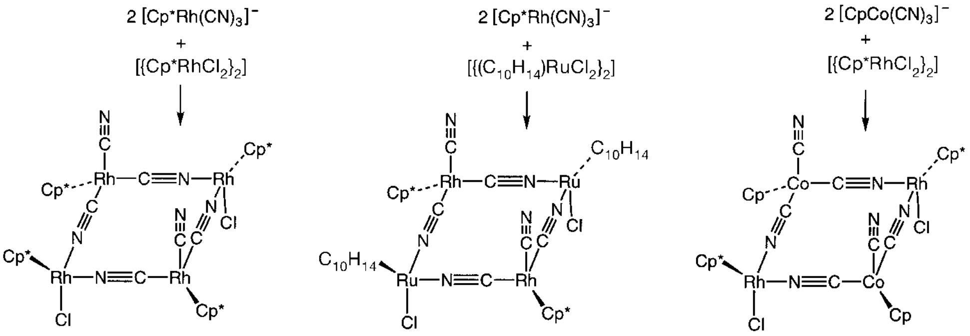
Solid-state coordination polymers[1] and molecular coordination ensembles[2–4] are typically constructed with bifunctional organic ligands such as 4,4'-bipyridine, and the vertices of the compounds are often square-planar or tetrahedral metal centers. An important advance in this area would involve the use of most common geometry for transition metals, the octahedron. Octahedral building blocks would allow the assembly of cube-shaped structures. Here we report the realization of this goal by the synthesis of a cubic array of cyano-linked[5] metal octahedra, a subunit of the polymeric hexacyanometalates. Prussian Blue complexes[6] such as $Fe_4[Fe(CN)_6]_3$ are polymeric by virtue of the sixfold bridging of the octahedral $[M(CN)_6]^{n-}$ subunits. In our approach, we have replaced three of these CN groups with a cyclopentadienyl ligand, which blocks one face of the octahedron. Polymerization is thus inhibited, and a family of cages with boxlike architectures results.



3 **4** **5**

Scheme 1. Assembly of $M_2M'_2(CN)_4$ squares.

The tricyanometalates $Et_4N[Cp^*Rh(CN)_3]$ (**1**)[7] and $K[CpCo(CN)_3]$ (**2**)[8] were employed to prepare a series of molecular squares ($Cp^* = C_5Me_5$, $Cp = C_5H_5$). Thus, **1** reacts with $[Cp^*RhCl_2]_2$ (CH_2Cl_2 solution, 25 °C, 2 h) to give **3**, which was isolated as orange crystals after purification on Sephadex LH-20 (Scheme 1). The two-line ^1H NMR spectrum of **3** indicates that the Rh–C bonds are retained in the assembly process. Although other $M_4(CN)_4$ squares are known,[9] the $2M(CN)_2 + 2M'$ route is novel.[10] The complex $[(cymene)RuCl_2]_2$ (cymene = 4-isopropyltoluene) reacts with **1** to give **4**. The ^1H NMR signal of C_5Me_5 group in **4** matches one of the signals of **3** and is assigned to the $Cp^*Rh(\mu\text{-}CN)_2(CN)$ moiety. A Co_2Rh_2 square **5** was prepared analogously with $[CpCo(CN)_3]^-$; in **5**, the Rh center is bound to the N atom of the cyanide ion. A single-crystal X-ray diffraction study confirmed the structure of **3** (Figure 1).[11]

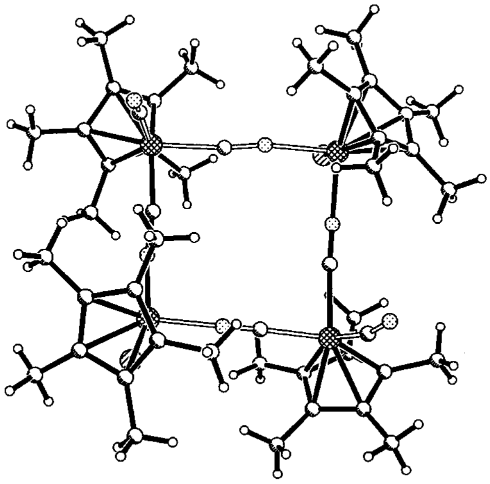


Figure 1. ORTEP plot of the structure of **3** with thermal ellipsoids drawn at the 50% probability level.

It is probable that many kinds of molecular objects could be prepared by using $[(C_5R_5)M(CN)_3]^-$ as metalloligands. Of particular interest are "molecular boxes" of the type $[(C_5R_5)_8M_8(\mu\text{-}CN)_{12}]$ in which metal centers occupy all eight corners. Molecular models show that Cp*–Cp* steric interactions would inhibit the assembly of the cubic cage $[Cp^*_8M_8(CN)_{12}]$; however, such boxlike architectures could be realized if half of the Cp* ligands were replaced by the smaller Cp groups.

The synthesis of the box was effected by removal of the chloride ligands from **5** with $AgPF_6$ (Scheme 2; MeCN solution, 25 °C, 12 h). According to NMR measurements, the yield is nearly quantitative. Note that all twelve μ-CN units are provided by the two $[Co_2Rh_2(CN)_6]$ precursors without the need to break any M–C bonds. The 500 MHz ^1H NMR spectrum of the product is simple: it consists of one signal

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