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Novel Routes to Heteronuclear Metal Clusters Containing Rhodium

F. G. A. Stone

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Novel routes to heteronuclear metal clusters containing rhodium

By F. G. A. Stone, F.R.S.

*Department of Inorganic Chemistry, University of Bristol, Bristol BS*8 1*TS, U.K.*

Logical methods for preparing small metal clusters with heteronuclear metal–metal bonds can be devised by appreciating the isolobal relationships that exist between certain metal ligand combinations and organic fragments. Thus the group $W(CO)_2(\eta\text{-}C_5H_5)$ has frontier orbitals of similar pattern to those of CH, while those of $Rh(CO)(\eta\text{-}C_5Me_5)$ and CH_2 are also similar. This paper shows how such ideas have been employed to generate compounds with bonds between rhodium and other metals.

Introduction

It has long been known that certain metal ligand fragments and organic species show to some degree similar reactivity patterns (e.g. $Pt(PR_3)_2$ and CH_2). Only recently, however, has the scope of these relations been fully appreciated, and an explanation given by Hoffmann (1982) in terms of the similarity of the frontier orbitals of the inorganic and organic groups. Two fragments are isolobal if the number, symmetry properties, approximate energy and shape of the frontier orbitals, and the number of electrons in them, are similar. By reference to Hoffmann's lecture (1982), it will be seen that the CH_2 or carbene moiety is isolobal with several metal ligand systems, e.g. PtL_2, $Rh(CO)(\eta\text{-}C_5Me_5)$, $Fe(CO)_4$, $Mn(CO)_2(\eta\text{-}C_5H_5)$, $Cr(CO)_5$, $Cr(CO)_2(\eta\text{-}C_6H_6)$, formally derived by removing electron-pair donor ligands L from an octahedral complex ML_6. Similarly, a carbyne fragment CR is isolobal with the species $W(CO)_2(\eta\text{-}C_5H_5)$ (W, d^5, ML_5), $RhR(\eta\text{-}C_9H_7)$† (Rh, d^7, ML_4), and $Co(CO)_3$ (Co, d^9, ML_3). These relations allow designed syntheses of compounds with heteronuclear metal–metal bonds, rather than the *ad hoc* preparative procedures previously employed. Because of time limitations, I shall restrict discussion to compounds involving rhodium.

The alkylidyne compound $[W{\equiv}CC_6H_4Me\text{-}4(CO)_2(\eta\text{-}C_5H_5)]$

The compound $[RC{\equiv}W(CO)_2(\eta\text{-}C_5H_5)]$ ($R = C_6H_4Me\text{-}4$ in the formulae) reacts with low-valent metal complexes in a similar manner to an alkyne, a property first exploited by us in reactions involving platinum.‡ Compounds **1** and **2** illustrate our early results, which subsequently led Hoffmann (1982) to point out the frontier orbital relation between $W(CO)_2(\eta\text{-}C_5H_5)$ and CR, following our intuitive ideas for synthetic work.

In the context of rhodium chemistry, the indenyl compound $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ reacts with the alkylidynetungsten complex to afford **3**. Treatment of the latter with $[Fe_2(CO)_9]$ gives the trimetal cluster **4**. Isolobal relationships allow **3** to be regarded as a dimetallacyclopropene, and **4** as a trimetallatetrahedrane. Compound **4** is perhaps the first example of a cluster species involving three metals each of which belongs to a different transition element series.

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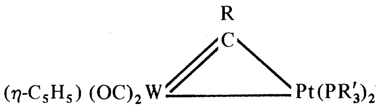
† $\eta\text{-}C_9H_7$ = the indenyl ligand.

‡ References to our experimental results are given in the appendix.

Treatment of **3** with $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ in toluene at *ca.* 60 °C affords the dirhodium-tungsten cluster **5**. Compound **6** is another species with a μ_3-CRh_2W core. It is prepared in a two-step synthesis, the first of which involves reacting $[W{\equiv}CR(CO)_2(\eta\text{-}C_5H_5)]$ with $[Rh(acac)(CO)_2]$ (acac = acetylacetonate) at room temperature to produce **7**. In the second



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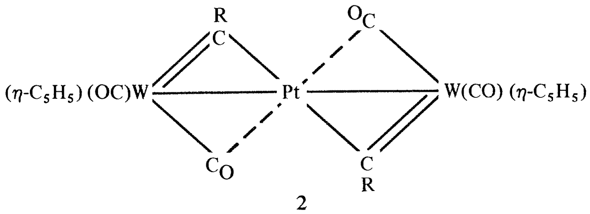

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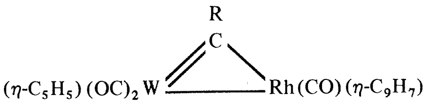

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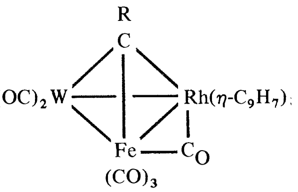

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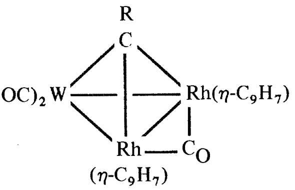

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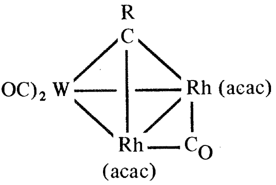

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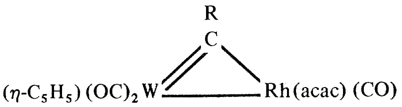

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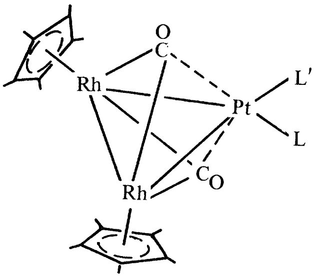
step, **7** is treated with $[Rh(acac)(C_2H_4)_2]$. The latter readily releases ethylene, so that a Rh(acac) fragment adds to the dimetallacyclopropene ring system, yielding the trimetal compound **6**. The principles underlying the preparation of **4**–**6** have been applied to several other systems so that these processes provide a general route to compounds having μ_3-$CM'M''W$ or μ_3-CM_2W core structures.

The compound $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$

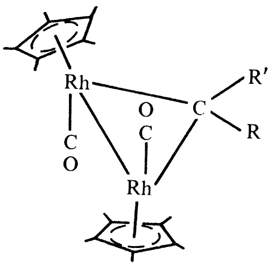
Jones *et al.* (1978) found that reduction of $[Rh(CO)_2(\eta\text{-}C_5H_5)]$ with sodium amalgam in tetrahydrofuran afforded, *inter alia*, the trirhodium anion $[Rh_3(\mu_3\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2]^-$. This observation stimulated Pinhas *et al.* (1980) to examine the bonding in the anion in relation to its structure. Several interesting results came from this study. The trirhodium species may be regarded as an adduct of the unknown molecule $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ (isolobal with ethylene) and $[Rh(CO)_2]^-$ (isolobal with CH_2). Moreover, $[Rh_3(\mu_3\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2]^-$

is clearly related to Herrmann's (1982) carbene bridged complexes $[Rh_2(\mu\text{-}CR_2)(CO)_2(\eta\text{-}C_5H_5)_2]$. Furthermore the latter and the trirhodium anion have similar ring-bonding to that of cyclopropane.

Whereas $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ has not yet been isolated, its analogue $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ has been prepared by Nutton & Maitlis (1979). Moreover, the $\eta\text{-}C_5Me_5$ and $\eta\text{-}C_5H_5$ derivatives are similar in formally containing Rh=Rh double bonds. Or, more precisely (Pinhas *et al.* 1980), both molecules have a $2b_2$ orbital like the π^* orbital of ethylene, and available for acceptance of electrons from a nucleophilic fragment.

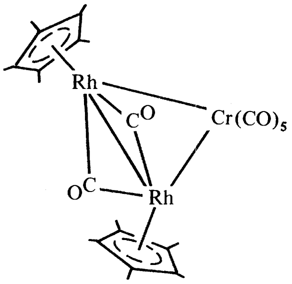


	L	L'
8*a*	cyclo-C_8H_{12}	
8*b*	CO	PPh_3
8*c*	CO	CO



	R	R'
9*a*	H	H
9*b*	CF_3	CF_3
9*c*	H	$CH{:}CH_2$

The isolobal relationships existing between $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ and C_2H_4, or between $Rh(CO)(\eta\text{-}C_5Me_5)$ and CH_2, have guided us in the preparation of several complexes with bonds between rhodium and other transition metals. Thus $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ would be expected to combine with those metal fragments (e.g. $Pt(PR_3)_2$, $Fe(CO)_4$) that bond ethylene, and trimetal complexes should exist containing a $Rh(CO)(\eta\text{-}C_5Me_5)$ fragment bridging metal–metal bonds that without this added moiety would formally have double-bond character.



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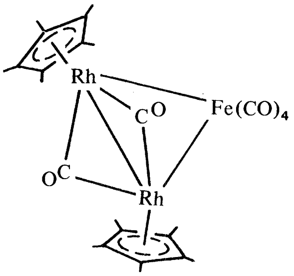

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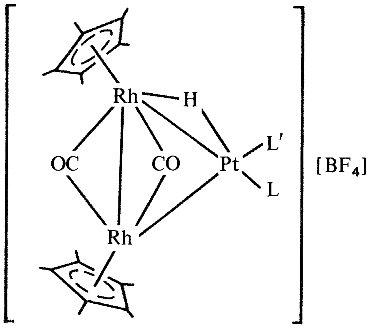
In the context of these ideas, the dirhodiumplatinum compounds **8** have been prepared by treating $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ with low-valent platinum complexes. In related work it was shown that the dirhodium compound reacts with diazoalkanes to afford the bridged alkylidene complexes **9**. Compounds **8** and **9** may be regarded as trimetalla- and dimetalla-cyclopropanes, respectively. Related to **8** are the trimetal compounds **10** and **11**, both obtained from $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ by addition of the carbene-like fragments $Cr(CO)_5$ and $Fe(CO)_4$, respectively. In compounds **8**–**11**, the CO ligands are either terminally bound (**9**), bridge two metal centres (**10**), or asymmetrically bridge three metal atoms (**8**). However, it is important to recognize that transformations between bridging and non-bridging carbonyl groups, a common feature of metal carbonyl chemistry, do not cause a major perturbation of the nature of the frontier orbitals in the metal fragments (Hoffmann 1982). Indeed, in solution **11** exists as a mixture of tautomers, involving an equilibrium between molecules with the structure shown and others with two semi-bridging and one triply-bridging CO ligands.

Perhaps the most spectacular example of the similarity in the coordination behaviour of $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ and ethylene is provided by the pentanuclear metal complex $[Pt\{Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2\}_2]$ (**12**) obtained by reacting the dirhodium compound with $[Pt(C_2H_4)_3]$. Two crystalline forms (monoclinic and orthorhombic) of **12** have been studied



L	L'
cyclo-C_8H_{12}	
CO	CO
CO	PPh_3

13

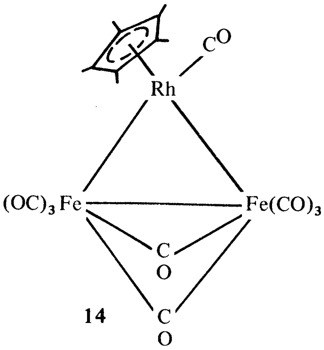
by X-ray diffraction. In both forms the four rhodium atoms are disposed around the platinum in an essentially tetrahedral environment, with the dihedral angles between the $PtRh_2$ planes being 90° (orthorhombic) and 100° (monoclinic). The four CO ligands, in addition to bridging the Rh–Rh vectors, weakly interact with the platinum atom; a feature that persists in solution, as deduced from ^{195}Pt–^{13}C coupling observed in the ^{13}C n.m.r. spectrum.

No X-ray diffraction studies have been made on molecules $[M(C_2H_4)_2]$, since they have only a fleeting existence. However, a family of stable compounds $[Pt(alkyne)_2]$ is known (Boag *et al.* 1980) and have structures in which the four ligated carbon atoms adopt a pseudo-D_{2d} arrangement around the platinum atom, as do the four rhodium atoms in **12**. For the hypothetical molecule $[Ni(C_2H_4)_2]$, calculations (Rösch & Hoffmann 1974) indicate only a small energy difference between D_{2d} and D_{2h} structures, because the ethylene π^* and metal d orbitals are far apart in energy and non-degenerate perturbation theory predicts similar stabilization. However, where the energy separation between the orbitals is small, as might be expected for the $2b_2$ orbitals of the two $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ moieties and the 5d orbitals of platinum, there would be a preference for a D_{2d} structure, as is observed. However, too much reliance should not be placed on these considerations because D_{2h} symmetry for the core metal atoms of **12** would result in steric crowding of the $\eta\text{-}C_5Me_5$ groups.

Protonation of the compounds **8** with HBF_4 in diethyl ether affords the salts **13**. These are interesting in several respects. In the context of isolobal relationships they are similar to edge-protonated cyclopropanes, the $[Pt(H)L_2]^+$ fragment being isolobal with CH_3^+. The salts **13** have structures in which the CO ligands bridging the Rh–Rh vectors do not triply bridge to the platinum to the same degree as do the corresponding CO groups in the neutral species **8**. In solution, the salts undergo dynamic behaviour involving rotation of the $Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2$ fragment about an axis through the platinum and the midpoint of the Rh=Rh unit, while the $Pt(H)L_2$ moiety retains its integrity at all times.

The rhodium fragment $Rh(CO)(\eta\text{-}C_5Me_5)$

The species $Rh(CO)(\eta\text{-}C_5Me_5)$ is isolobal with CH_2, because it is effectively a fragment RhL_4 (Rh^I, d^8) like $Fe(CO)_4$ (Fe^0, d^8) (Hoffmann 1982). Hence the existence of the compound **14** is not surprising; a trimetal cluster we have obtained from the reaction between $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ and $[Fe_2(CO)_9]$ in tetrahydrofuran (thf). It is interesting to compare **14** with the isolobally related methylene adduct of the $Fe_2(CO)_8$ molecule, namely $[Fe_2(\mu\text{-}CH_2)(CO)_8]$ (Sumner 1980).



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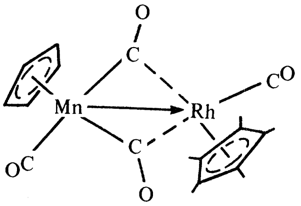

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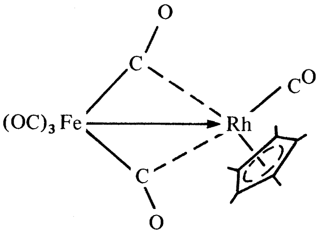

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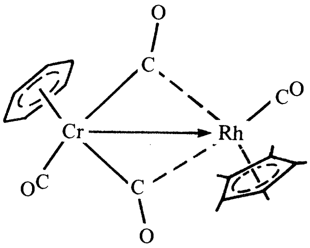

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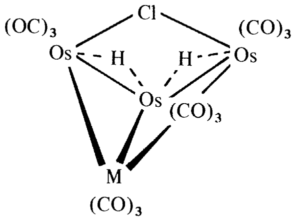
The compound $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ undergoes an interesting group of reactions with the species $[Mn(CO)_2(thf)(\eta\text{-}C_5H_5)]$, $[Fe(CO)_4(thf)]$ and $[Cr(CO)_2(thf)(\eta\text{-}C_6H_6)]$. By release of the weakly coordinated thf molecules, these three reagents afford the carbene-like metal–ligand moieties $Mn(CO)_2(\eta\text{-}C_5H_5)$, $Fe(CO)_4$ and $Cr(CO)_5$. The products of the three reactons are the bimetallic compounds **15–17**, the formation of which has resulted in the transfer of a CO group from rhodium to Mn, Fe and Cr, respectively. Although not metal clusters, in the normal definition, the complexes **15–17** illustrate the isolobal concept, which so usefully links inorganic and organic chemistry. All three compounds contain the $Rh(CO)(\eta\text{-}C_5Me_5)$ fragment to which an electron pair has been donated from the h.o.m.o. of the molecules $[Mn(CO)_3(\eta\text{-}C_5H_5)]$, $[Fe(CO)_5]$ and $[Cr(CO)_3(\eta\text{-}C_6H_6)]$, an orbital that is probably metal-centred (Lichtenberger & Fenske 1976). Consequently, **15–17** are akin to ylides $R_3P \rightarrow CH_2$: in the three metal complexes excess charge on the rhodium is dissipated via the semi-bridging carbonyls, whereas with ylides the canonical form $R_3P{=}CH_2$ is important.

Future prospects

The above brief account of a small portion of our recent work will, I hope, indicate the usefulness of approaching the synthesis of compounds with metal–metal bonds by giving due regard to the frontier orbital similarities of the metal ligand fragments involved. The potential of this approach is illustrated by two very recent researches, which serve to close this discussion.

Again by reference to Hoffmann (1982) it will be seen that a T-shaped ML_3 (M, d^8) fragment is isolobal with CH_3^+ or CH_2. Such fragments are available for Rh^I or Ir^I by release of $NH_2C_6H_4Me$-4 from the complexes $[MCl(CO)_2(NH_2C_6H_4Me\text{-}4)]$ (M = Rh or Ir). Accordingly, reactions have been studied between the latter and $[Os_3(\mu\text{-}H)_2(CO)_{10}]$, a molecule known to add carbene groups readily. The products obtained, **18**, have a 'butterfly' arrangement of the metal atom core, with the wingtips bridged by Cl and hydrido ligands in the positions indicated. These compounds do not contain T-shaped $MCl(CO)_2$ 'carbene' fragments, but $M(CO)_3$ groups isolobal with CH. This prompts a cautionary comment about isolobal mapping. There is no guarantee that a synthesis based on a correlation between the isolobal nature of two groups (e.g. $RhCl(CO)_2$ and CH_2) will result in products with similar structures. Kinetic and thermodynamic factors will influence the structure of the final products.



	M
(18*a*)	Rh
(18*b*)	Ir

We have stressed earlier the usefulness of $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ as a building block in metal cluster chemistry. The cobalt analogue is known, and a good method of synthesis has recently been developed (Beevor 1981). This molecule has been shown (Cirjak *et al.* 1980) to add a number of photolytically generated metal fragments, thereby affording a variety of heteronuclear trimetal complexes. Clearly this important work is related to that discussed in this paper.

Of particular interest would be mixed-metal species containing formally Co=Rh bonds, because addition of other metal ligand fragments to these molecules should afford tri- or tetra-nuclear clusters with three different transition elements. With this in mind, what is conceptually evident is the possible dimerization of $Co(CO)(\eta\text{-}C_5Me_5)$ and $Rh(CO)(\eta\text{-}C_5Me_5)$ fragments to give $[CoRh(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (**19**). This we have accomplished by reacting $[Co(C_2H_4)_2(\eta\text{-}C_5Me_5)]$ with $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ because the former can scavenge a CO group from the latter. Compound **19** has recently been shown to combine with several 'carbene-like' metal–ligand fragments, e.g. $Mo(CO)_5$, $Fe(CO)_4$, and $Pt(cyclo\text{-}C_8H_{12})$, to afford trimetal clusters.

References

Beevor, R. G., Frith, S. A. & Spencer, J. L. 1981 *J. organometall. Chem.* **221**, C25.
Boag, N. M., Howard, J. A. K., Green, M., Grove, D. M., Spencer, J. L. & Stone, F. G. A. 1980 *J. chem. Soc. Dalton Trans.*, p. 2170.
Cirjak, L. M., Huang, J.-S., Zhu, Z.-H. & Dahl, L. F. 1980 *J. Am. chem. Soc.* **102**, 6623.
Herrmann, W. A. 1982 *Adv. organometall. Chem.* **20**, 159.
Hoffmann, R. 1982 *Les Prix Nobel 1981*. Stockholm: Almqvist & Wiksell.

Jones, W. D., White, M. A. & Bergman, R. D. 1978 *J. Am. chem. Soc.* **100**, 6770.
Lichtenberger, D. L. & Fenske, R. F. 1976 *J. Am. chem. Soc.* **98**, 50.
Nutton, A. & Maitlis, P. M. 1979 *J. organometall. Chem.* **166**, C21.
Pinhas, A. R., Albright, T. A., Hofmann, P. & Hoffmann, R. 1980 *Helv. chim. Acta* **63**, 29.
Rösch, N. & Hoffmann, R. 1974 *Inorg. Chem.* **13**, 2656.
Sumner, C. E., Riley, P. E., Davis, R. E. & Pettit, R. 1980 *J. Am. chem. Soc.* **102**, 1752.

APPENDIX

The articles listed below describe our own experimental results reviewed in this symposium.

Compounds **1** *and* **2**:
Ashworth, T. V., Howard, J. A. K. & Stone, F. G. A. 1979 *J. chem. Soc. chem. Commun.*, p. 42.
Ashworth, T. V., Howard, J. A. K. & Stone, F. G. A. 1980 *J. chem. Soc. Dalton Trans.*, p. 1609.
Ashworth, T. V., Chetcuti, M. J., Howard, J. A. K., Stone, F. G. A., Wisbey, S. J. & Woodward, P. 1981 *J. chem. Soc. Dalton Trans.*, p. 763.

Compounds **3**–**5**:
Green, M., Jeffery, J. C., Porter, S. J., Razay, H. & Stone, F. G. A. 1982 *J. chem. Soc. Dalton Trans.* (In the press.)

Compounds **6** *and* **7**:
Chetcuti, M. J., Chetcuti, P. A. M., Jeffery, J. C., Mills, R. M., Mitrprachachon, P., Pickering, S. J., Stone, F. G. A. & Woodward, P. 1982 *J. chem. Soc. Dalton Trans.*, p. 699.

Compounds **8** *and* **9**:
Green, M., Mills, R. M., Pain, G. N., Stone, F. G. A. & Woodward, P. 1982 *J. chem. Soc. Dalton Trans.*, p. 1309.

Compound **10**:
Barr, R. D., Green, M. & Stone, F. G. A. *J. chem. Soc. Dalton Trans.* (Submitted.)

Compounds **11**, **14**, **15** *and* **16**:
Aldridge, M. L., Green, M., Howard, J. A. K., Pain, G. N., Porter, S. J., Stone, F. G. A. & Woodward, P. 1982 *J. chem. Soc. Dalton Trans.*, p. 1333.

Compound **12**:
Green, M., Howard, J. A. K., Pain, G. N. & Stone, F. G. A. 1982 *J. chem. Soc. Dalton Trans.*, p. 1327.

Compound **13**:
Green, M., Mills, R. M., Pain, G. N., Stone, F. G. A. & Woodward, P. 1982 *J. chem. Soc. Dalton Trans.*, p. 1321.

Compound **17**:
Barr, R. D. Bristol University, unpublished results.

Compound **18**:
Farrugia, L. J., Orpen, A. G. & Stone, F. G. A. 1982 *Polyhedron.* (In the press.)

Compound **19**:
Hankey, D. R. Bristol University, unpublished results.