

Metallomacrocycles: novel amphoteric macrocycles with metal ions and traditional Lewis bases as binding sites

Alan L. Balch

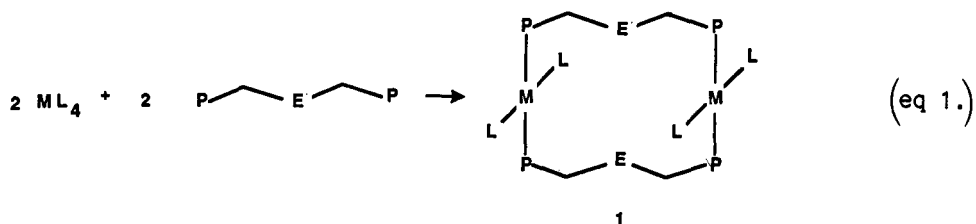
Department of Chemistry, University of California, Davis, CA 95616, USA

Abstract - A new group of macrocycles has been prepared by the combination of functionalized diphosphines such as bis(diphenylphosphinomethyl)phenylarsine with d^8 and d^{10} metal complexes to give cyclic molecules with two metal ions and two Lewis bases (nitrogen or arsenic) surrounding a central void. Examples of the binding of cations, neutral molecules, and anions to these metallomacrocycles are described.

INTRODUCTION

Macrocycles with multiple Lewis base binding sites are well known and chemically useful species, particularly for the binding of cations (ref. 1). This conference is a demonstration of the interest and importance of these species. Recently a few examples of macrocycles containing several Lewis acid binding sites have been prepared, and their ability to complex anions has been investigated (ref. 2). Here, however, we are concerned with the formation and reactivity of another class of macrocycles, those which contain both Lewis acid and Lewis base binding sites within the same molecule. Clearly a major problem in the construction of such macrocycles is the need to keep the acid and base portions from reacting with one another.

Our work has focused on obtaining molecules with two transition metal or post transition metal ions and two Lewis base sites in a cyclic system, although other numbers of metal ions and Lewis bases could be targeted. The approach has used a functionalized diphosphine to coordinate the metal ions to produce the desired metallomacrocycles **1** as shown in eq 1. The diphosphine provides the Lewis base



binding sites, E, while the transition metal ions, M, provide the Lewis acid binding sites. In order to prevent E from binding M, several strategies can be employed. Geometric constraints can be built into the diphosphine which will disfavor chelation. The electronic structure of E can also be manipulated so that it remains unbound to M. In this case, it is useful to take into account the relative binding preferences of Group 15 donors. Toward soft metal ions that binding order is $N \langle P \rangle \text{As} \rangle \text{Sb} \rangle \text{Bi}$ (ref. 3). Thus soft metal ions prefer to bind phosphorus over other Group 15 donors. Consequently, using soft metal ions for M and nitrogen or arsenic donors for E, we should be able to construct the desired metallomacrocycles **1**.

To date, our work has focused on two diphosphines, 2,6-bis(diphenylphosphino)pyridine, $(\text{Ph}_2\text{P})_2\text{py}$ (ref. 4), and bis(diphenylphosphinomethyl)phenylarsine, dpma (ref. 5). For metal ions, we have concentrated on d^8 and d^{10} ions which prefer planar or linear coordination. These low-coordinate metals bring with them few other ligands to crowd the center of the macrocycle. Additionally, their coordination unsaturation is requisite for substrate binding. Here we describe the formation of a number of metallomacrocycles **1** and their ability to complex cations, neutral molecules, and anions through a unique array of Lewis acid/base interactions. X-ray crystallographic studies play a key role in defining the structures of these novel macrocycles and their adducts.

METALLOMACROCYCLES DERIVED FROM 2, 6-BIS(DIPHENYLPHOSPHINO)PYRIDINE

The structures of three empty metallomacrocycles obtained from the reaction of $(\text{Ph}_2\text{P})_2\text{py}$ with palladium(II) and platinum(II) halo complexes are shown in Figure 1 (ref. 6). The two platinum complexes conform to the desired structure 1 while the palladium complex is a trimer with a quite irregular geometry. The differences between the complexes in Figure 1 emphasize some of the structural features of these metallomacrocycles which need to be regulated, but which can be difficult to control. The variation in ring size here is one. The palladium complex forms as a trimer in high yield and has defied all attempts to convert it into a dimer. The two platinum complexes differ in the local coordination of phosphorus at platinum; cis in one case, trans in the other. Here, by suitable choice of the ancillary ligands, some regulation of trans rather than cis geometry is possible.

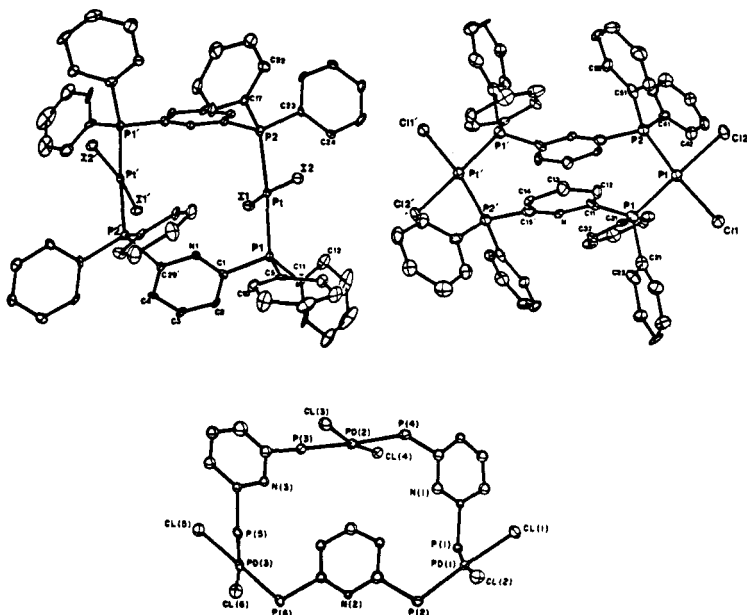


Figure 1. Structures of three empty metallomacrocycles with $(\text{Ph}_2\text{P})_2\text{py}$ backbones.

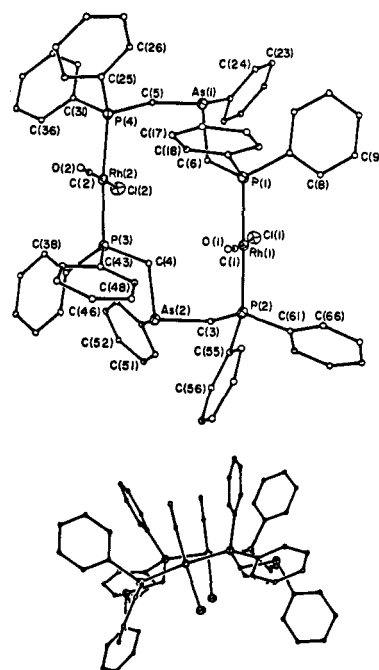
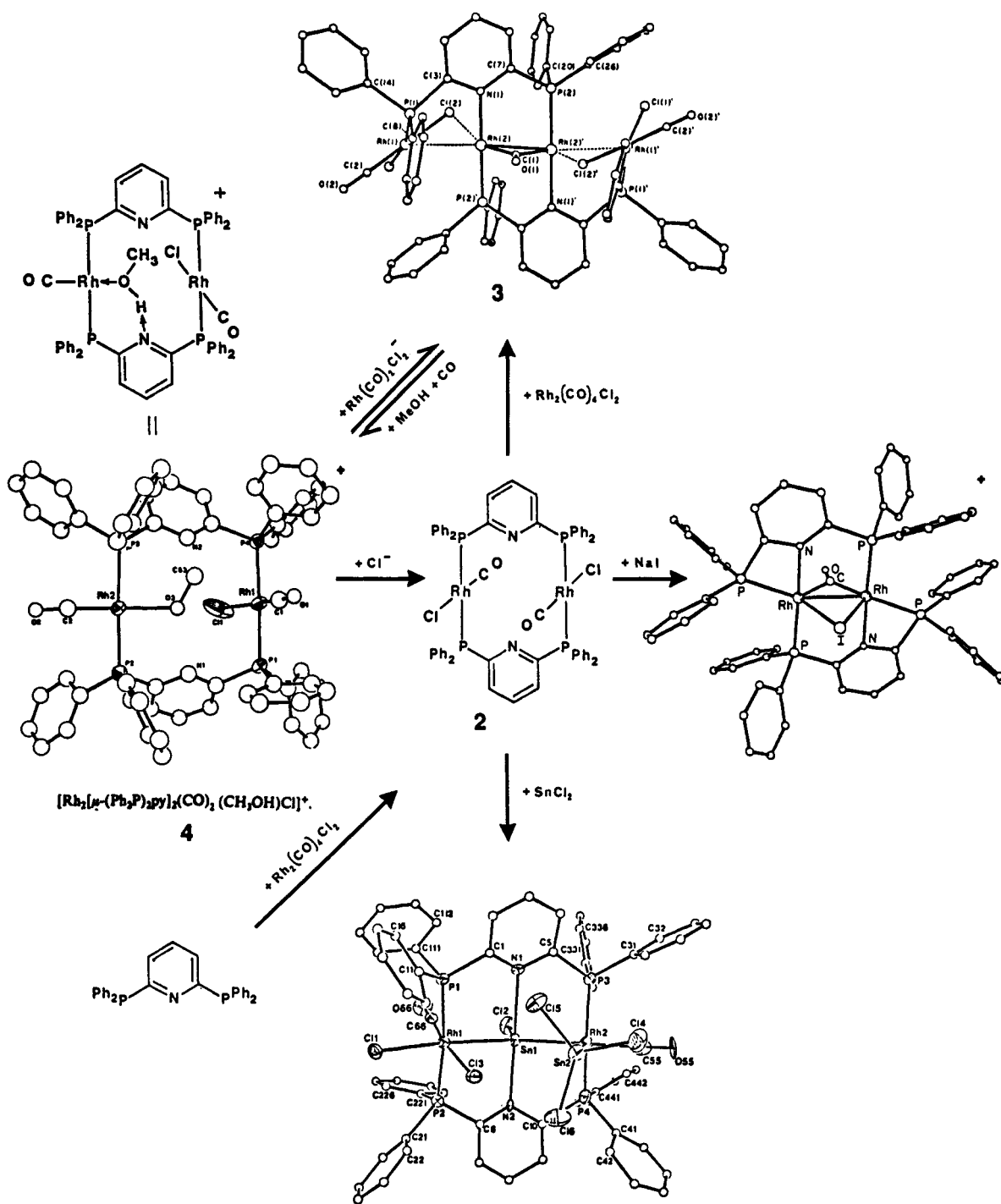


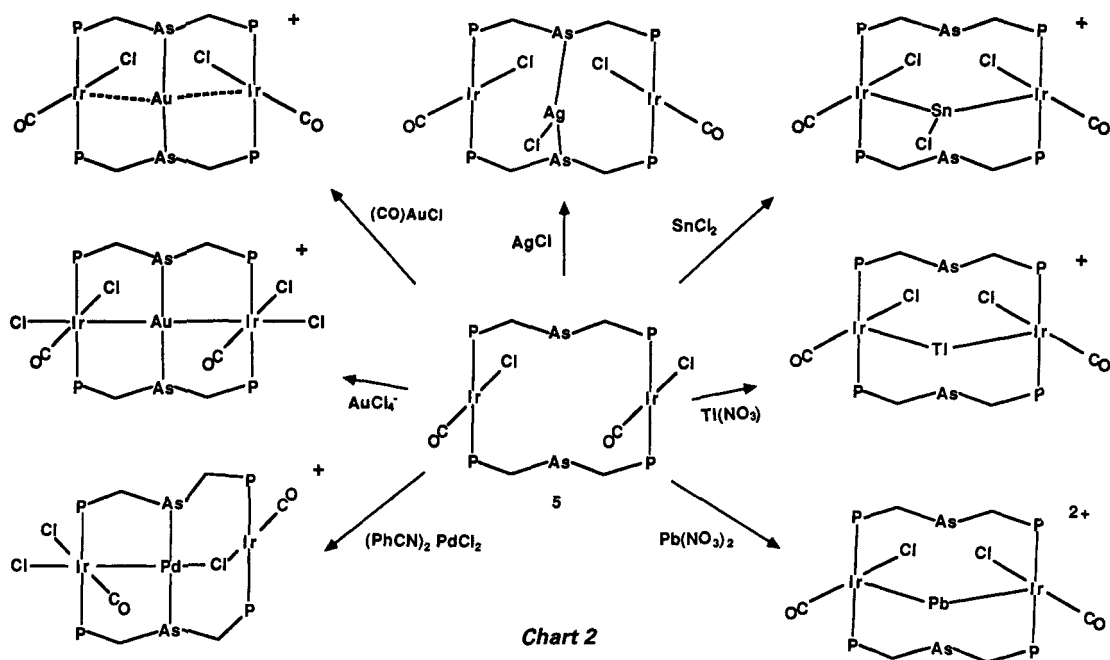
Figure 2. Two views of the metallomacrocyclic, $\text{Rh}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2$.

The reactivity of metallomacrocycles of this type has been most extensively examined for the rhodium complex, $\text{Rh}_2\{(\text{Ph}_2\text{P})_2\text{py}\}_2(\text{CO})_2\text{Cl}_2$, **2** (ref. 7-10). Although this complex itself has not been crystallographically characterized, a number of its reaction products have been. Chart 1 shows these. The reaction with tin(II) chloride shown at the bottom is an example of binding of a metal ion (the binding of $\text{Sn}(1)$) which we expected would be characteristic of these metallomacrocycles (ref. 7). However, this behavior is actually quite rare probably because of the inflexibility of the $(\text{Ph}_2\text{P})_2\text{py}$ backbone. While this backbone assists in forming metalocycles by geometrically preventing chelation, it then forms metalocycles with a fixed M-M separation. For trans coordination as in **2**, that separation is ~ 5.2 Å. Attempts to add a rhodium ion to the center of **2** result in the rupture and realignment of the diposphine backbone seen in the reaction at the top of Chart 1 (ref. 9). Here an unexpected tetranuclear complex, **3**, is formed. The rupture and realignment reaction is also seen in the reaction of **2** with sodium iodide seen to the right of Chart 1 (ref. 10). Treatment of tetranuclear **3** with carbon monoxide in methanol causes a third rupture and realignment reaction, in this case a reversible one (ref. 8). The product **4** shows a novel example of a neutral molecule bound within a metallomacrocyclic. A methanol molecule coordinates $\text{Rh}(2)$ as a Lewis base through $\text{O}(3)$ while $\text{N}(1)$ acts as a hydrogen bond acceptor and further stabilizes the coordination of the methanol (ref. 8). Alcohols are generally weakly bound to soft metal ions such as rhodium(I). Here, however, structural characterization has been facilitated by the unique set of acid/base interactions that are possible within a metallomacrocyclic.



RHODIUM(I) AND IRIIDIUM(I) METALLOMACROCYCLES BASED ON BIS(DIPHENYLPHOSPHINOMETHYL)PHENYLARSINE

Because of the inflexibility of the $(\text{Ph}_2\text{P})_2\text{py}$ backbone, we turned our attention to the much more flexible dpma as a building block. Here, we no longer have geometric restraints to various possible forms of chelation. Fortunately, however, we can use the ability of a d^8 $\text{Rh}^{\text{I}}\text{-CO}$ or $\text{Ir}^{\text{I}}\text{-CO}$ fragment to direct phosphine ligands away from the coordination site trans to the carbon monoxide ligand to facilitate the formation of the desired metallomacrocycles. Thus dpma reacts with $\{\text{Rh}(\text{CO})_2\text{Cl}\}_2$ or $\text{Ir}(\text{CO})_2\text{Cl}(\text{p-toluidine})$ to form $\text{Rh}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2$ or $\text{Ir}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2$ (ref. 5). The structure of the former, as determined crystallographically, is shown in Figure 2.



Crystallographically characterized complexes of 5

Chart 2 summarizes some of the metal ion binding displayed by $\text{Ir}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2$, **5**. In the reaction with solid silver chloride, **5** acts as a simple bidentate diarsine ligand. No Ir-Ag bonding is present, the $\text{Ir}\cdots\text{Ag}$ distances are 3.356(1) and 3.362(1) Å (ref. 11, 12). The reaction with $\text{ClAu}(\text{CO})$ gives a somewhat similar complex, but the gold ion is closer to the iridium, with Au-Ir distances of 3.059(1) and 3.012(1) Å (ref. 12).

The reactions of **5** with the main group ions, Tl^+ , Pb^{2+} and SnCl^+ (from SnCl_2), are perhaps the most surprising (ref. 14). The only bonding to these ions occurs through the iridium atoms. For example in the thallium complex the Ir-Tl distances are 2.958(1) and 2.979(1) Å while the $\text{Tl}\cdots\text{As}$ separations are greater (3.295(3), 3.308(3) Å). Moreover, the arsenic lone pairs point 40° away from the thallium. The ability to bond Tl^+ and Pb^{2+} in this fashion is a unique property of this sort of cyclic molecule. No interaction occurs between these ions and the corresponding mononuclear complex $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$. These complexes show characteristic electronic spectra. Figure 3 compares the electronic spectra of the empty metallomacrocyclic **5** with its Tl^+ and Pb^{2+} complexes. These show intense absorptions in the visible and are particularly remarkable since Tl^+ and Pb^{2+} complexes are generally colorless. The adducts also display intense emission spectra from fluid solution at room temperature. These factors, combined with the reversible nature of Tl^+ and Pb^{2+} binding, suggest that the metallomacrocyclic **5** could be developed as an analytical reagent for these ions. In this context it is important to note that **5** shows no reactivity toward the alkali metal ions, and that it readily distinguishes between the similarly sized Tl^+ and Rb^+ .

The reactions with $(\text{C}_6\text{H}_5\text{CN})_2\text{Pd}_2$ (ref. 5) and AuCl_4 (ref. 15) demonstrate cases of transfer of ligands from one metal to another in complexation by **5**. In effect one (in the case of Pd) or two (in the case of Au) of the iridium centers undergoes oxidative-addition of a M-Cl bond. The formation of one or two new metal-metal bonds results.

BIS(DIPHENYLPHOSPHINOMETHYL)PHENYLARSINE BASED METALLOMACROCYCLES WITH d^{10} METALS

The linear coordination characteristic of d^{10} metal ions, Au^+ , Ag^+ , Hg^+ , should make these excellent candidates for M in **1**. To date, however, attempts to prepare a gold metallomacrocyclic have not succeeded. Only a rather ordinary chelate compound, $\text{Au}(\text{dpma})_2^+$, with tetrahedral AuP_4 coordination has been obtained.

The behavior of Hg^{2+} is much more promising. Addition of dpma to a solution of $\text{Hg}(\text{O}_3\text{SCF}_3)_2$ in methanol gives the complex $[\text{Hg}_2(\mu\text{-dpma})_2(\text{CH}_3\text{OH})_2(\text{O}_3\text{SCF}_3)_2][\text{PF}_6]_2$. The cation of this is shown in Figure 4. The desired metallomacrocyclic has formed. The

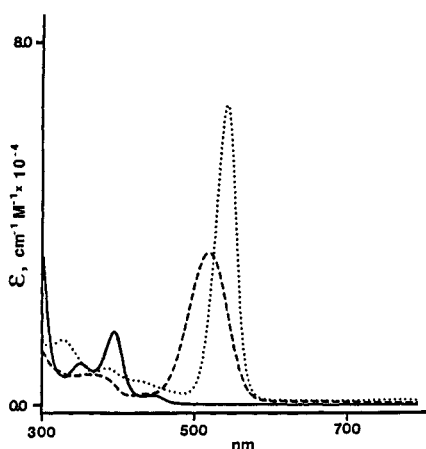


Figure 3. The electronic absorption spectra of equimolar dichloromethane solutions of: $\text{Ir}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2$, solid line; $[\text{Ir}_2\text{Tl}(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2]^+$, dashed line; $[\text{Ir}_2\text{Pb}(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2]^{2+}$, dotted line.

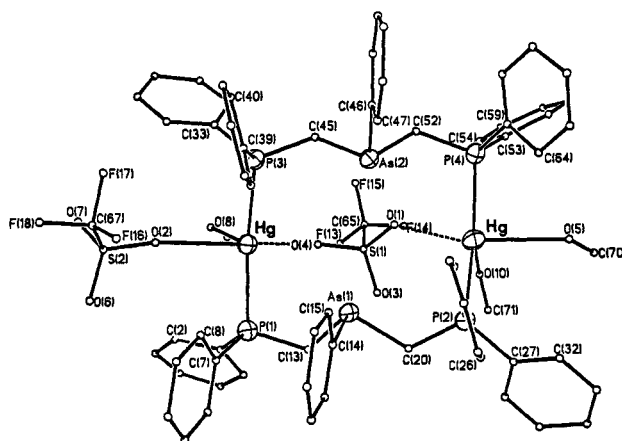


Figure 4.

The cation in $[\text{Hg}_2(\mu\text{-dpma})_2(\text{CH}_3\text{OH})_3(\text{O}_3\text{SCF}_3)_2][\text{PF}_6]_2$.

arsenic atoms are uncoordinated while the two mercury atoms have a linear PHgP coordination which is supplemented by weak binding to additional methanol molecules and the trifluoromethylsulfonate anions, one of which forms a bridge between the two mercury ions. Further studies on the reactivity of this mercury-based metallomacrocyclic are in progress.

SUMMARY

These studies demonstrate that metallomacrocycles can be obtained and they have the ability to complex a variety of substrates. The construction of other metallomacrocycles with different numbers of M and E units, and with vastly different geometries can be anticipated. Since these may have both Lewis acid and Lewis base properties, they have considerable potential for developing very specific interactions with substrates.

Acknowledgements

I thank my coworkers Alan Fossett, Professor Mauro Ghedini, Professor Jeffrey Nagle, Dr. Marilyn Olmstead, Doug Oram, Phil Reedy, Steve Rowley and Dr. Fred Wood for their contributions, the National Science Foundation (Grant CHE8519557) for financial support and Johnson Matthey for a loan of rhodium and iridium salts.

REFERENCES

1. R.M. Izatt, J.J. Christensen, eds., *Synthetic Multidentate Macrocyclic Compounds*, Academic Press, New York (1978).
2. For examples, see T.J. Karol, J.P. Hutchinson, J.R. Hyde, H.G. Kuivila, J.A. Zubieta, *Organometallics*, **2**, 106 (1983). A.L. Beauchamp, M.J. Oliver, J.D. Wuest, B. Zacharie, *J. Am. Chem. Soc.*, **108**, 73 (1986).
3. S. Ahrland, J. Chatt, N.R. Davies, *Quart. Rev. Chem. Soc.*, **12**, 265 (1958).
4. G.R. Newkome, D.C. Hager, *J. Org. Chem.*, **43**, 947, (1978).
5. A.L. Balch, L.A. Fossett, M.M. Olmstead, D.E. Oram, P.E. Reedy, Jr., *J. Am. Chem. Soc.*, **107**, 5272, (1985).
6. F.E. Wood, J. Hvoslef, H. Hope, A.L. Balch, *Inorg. Chem.*, **23**, 4309 (1984).
7. A.L. Balch, H. Hope, F.E. Wood, *J. Am. Chem. Soc.*, **107**, 6939 (1985).
8. F.E. Wood, J. Hvoslef, A.L. Balch, *J. Am. Chem. Soc.*, **105**, 6986, (1983).
9. F.E. Wood, M.M. Olmstead, A.L. Balch, *J. Am. Chem. Soc.*, **105**, 6332 (1983).
10. A.L. Balch, L.A. Fossett, M.M. Olmstead, *Inorg. Chem.*, **25**, 4526 (1986).
11. A.L. Balch, M. Ghedini, D.E. Oram, P.E. Reedy, Jr., *Inorg. Chem.*, in press.
12. A.L. Balch, D.E. Oram, P.E. Reedy, Jr., unpublished results.
13. A.L. Balch, J.K. Nagle, D.E. Oram, P.E. Reedy, Jr., submitted for publication.
14. A.L. Balch, J.K. Nagle, M.M. Olmstead, P.E. Reedy, Jr., *J. Am. Chem. Soc.*, in press.
15. A.L. Balch, D.E. Oram, P.E. Reedy, Jr., *Inorg. Chem.*, in press.
16. A.L. Balch, L. A. Fossett, M.M. Olmstead, P.E. Reedy, Jr., *Organometallics*, **5**, 1929 (1986).
17. A.L. Balch, L.A. Fossett, R.R. Guimerans, M.M. Olmstead, P.E. Reedy, Jr., F.E. Wood, *Inorg. Chem.*, **25**, 1248, (1986).
18. A.L. Balch, L.A. Fossett, R.R. Guimerans, M.M. Olmstead, P.E. Reedy, Jr., *Inorg. Chem.*, **25**, 1397, (1986).