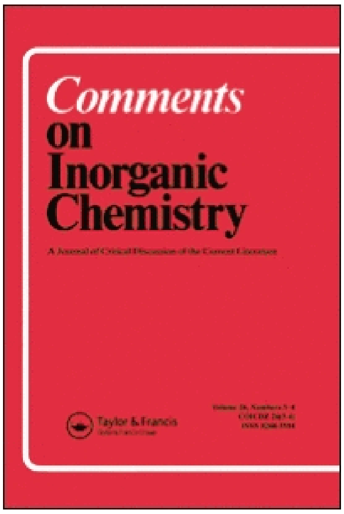

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New Applications of Weak Donor Atoms to Coordination, Organometallic and Materials Chemistry

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New Applications of Weak Donor Atoms to Coordination, Organometallic and Materials Chemistry

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Non-aqueous solvated transition metal cations are enjoying renewed popularity as precursors for new applications in molecular and materials chemistry. In two related projects, we are engaged in a general investigation of the syntheses, structures and reactivity of new compounds containing nitrile and ether ligands. A major effort is underway to synthesize homoleptic metal–metal bonded acetonitrile cations of second and third row metals for use in coordination and organometallic chemistry, photochemistry and materials chemistry. Dinuclear carboxylate, halide and halide–phosphine complexes are used to synthesize the metal–metal bonded acetonitrile cations $[M_2(MeCN)_{10}]^{4+}$ (M = Re, Rh). The unusual partially solvated species $[Mo_2^{IV,IV}(\mu\text{-}F)(MeCN)_8O_2]^{3+}$ was prepared from $MoCl_3(THF)_3$ in CH_3CN. Reactions of the bulky ether–phosphine ligand tris(2,4,6-trimethoxyphenyl)phosphine (TMPP) with the dinuclear cation $[Rh_2(MeCN)_{10}]^{4+}$ and with acetonitrile cations of 3d metals $[M(MeCN)_6]^{2+}$ (M = Co, Ni) produce bis–phosphine complexes of general formula $[M(PR_3)_2]^{n+}$ where $M = Co^{2+}, Ni^{2+}, Ni^{3+}, Rh^{2+}, Rh^{3+}$. Weakly interacting ether donors on the large phosphine ligand occupy open coordination sites in the solid state. Dissociation of the ether groups in solution is favored, as demonstrated by reactions of Rh(II) and Rh(I) TMPP complexes with CO and CNR. Reversible binding of CO is demonstrated in several systems. Applications of molecules with labile ether or nitrile ligands to the design of sensors, mixed metal oxides and polymers will be outlined.

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Key Words: *weak donor ligands, homoleptic nitrile complexes, ether–phosphine ligands, solvated dinuclear cations, mononuclear rhodium(II) complexes, phosphino-phenoxide ligands, reversible CO chemistry, polynitrile acceptors, σ-bonded TCNQ*

I. INTRODUCTION

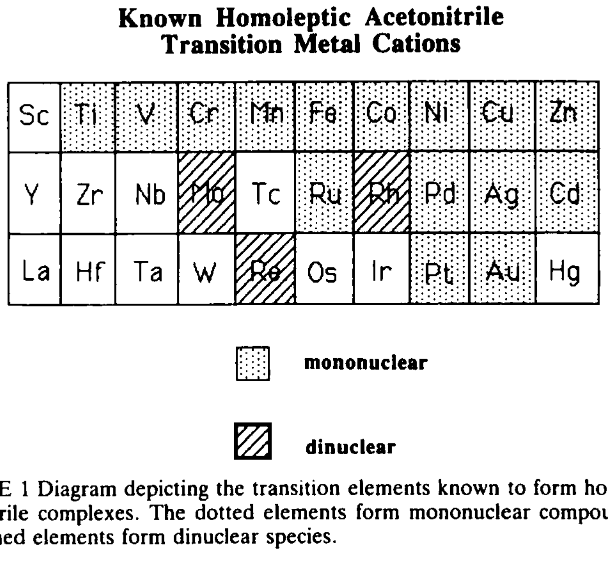
Nitriles and Ethers as Ligands

The use of donor solvents as temporary ligands for transition metals is a time-honored method for preparing reactive coordination and organometallic compounds.[1] Two common solvents used in this capacity are nitriles and ethers. Metal–nitrile complexes date from circa 1850 and are among some of the earliest coordination compounds to be thoroughly investigated by synthetic chemists and spectroscopists.[2] Nearly thirty years have elapsed since the publication of the first extensive reviews on the structures, spectral properties and reactivity of acetonitrile complexes, and although this area of classical coordination chemistry has seen much activity in the ensuing years, new applications of electrophilic nitrile complexes continue to be unearthed.[3] Interest in homoleptic acetonitrile complexes with non-coordinating anions is particularly keen due to their tendency to undergo nitrile dissociation in a variety of organic solvents to produce catalysts for the activation of C=C, C–C and C–H bonds.[3]

Several years ago, we set out to extend the class of homoleptic acetonitrile compounds to include unrepresented 4d and 5d metals. A comprehensive search of the literature revealed that most of the documented examples were of the first row elements (groups 4–12). Reports of related chemistry for the heavier transition metals, especially those of groups 5–9, were scarce by comparison. Syntheses of 3d metal acetronitrile cations with counterions such as $[SbF_6]^-$, $[BiF_6]^-$, $[AlCl_4]^-$ and $[ClO_4]^-$ were outlined in a series of papers in the late 1960's; these employ metal halide precursors together with various halide abstraction reagents.[4] An even earlier procedure involves oxidation of metal powder or filings with $NOBF_4$ in acetonitrile to yield the divalent mononuclear cations $[M(MeCN)_6]^{2+}$.[5] At the time we initiated our studies in 1988, homoleptic acetonitrile cations of the heavier elements were known for Ru(II), Pd(II), Pt(II), Ag(I), Au(I) and Cd(II) and Eu(III).[6,7]

Besides these, the dinuclear species formulated as $[Mo_2(MeCN)_8]^{4+}$ was postulated but not fully characterized.[8a,b] Later, Cotton and co-workers published the definitive synthesis and characterization of the Mo_2^{4+} complex.[8c,d] This article details several remarkably simple strategies for the synthesis and isolation of new *dinuclear* complexes stabilized entirely by acetonitrile ligands. The diagram in Fig. 1 depicts the current list of known homoleptic acetonitrile cations including those recently prepared for the first time in our laboratories and others.[8c,d,9] The acetonitrile complexes of Mo, Re and Rh of general formula $[M_2(MeCN)_{10}]^{4+}$ are members of a new homologous series of unbridged metal–metal bonded compounds that are proving to be very useful entry points into new coordination compounds and materials. This overview will focus primarily on applications discovered in our own laboratories.

Although there are no reports of transition metal cations stabilized entirely by ether ligands, tetrahydrofuran has been used extensively in coordination compounds to replace, typically, one to three stronger donor ligands.[1] For example, $VCl_3(THF)_3$ [10] and $MoCl_3(THF)_3$ [11] are excellent starting materials for the coordination chemistry of these elements. The use of THF as a good



Known Homoleptic Acetonitrile Transition Metal Cations

Sc	░ Ti	░ V	░ Cr	░ Mn	░ Fe	░ Co	░ Ni	░ Cu	░ Zn
Y	Zr	Nb	▨ Mo	Tc	░ Ru	▨ Rh	░ Pd	░ Ag	░ Cd
La	Hf	Ta	W	▨ Re	Os	Ir	░ Pt	░ Au	Hg

░ mononuclear

▨ dinuclear

FIGURE 1 Diagram depicting the transition elements known to form homoleptic acetonitrile complexes. The dotted elements form mononuclear compounds and the dashed elements form dinuclear species.

leaving group is also familiar to the organometallic chemist; the recent work of Jordan *et al.* in the development of the rich chemistry of $Cp_2Zr(R)(THF)^+$ species is a good illustration of this point.[12] In addition to relying on the ability of free ethers to replace stronger donors such as halides, one may design ligands with pendent ether groups to serve as "built-in" solvent molecules.[13] In this category are ether–phosphines, ligands that offer several advantages that set them apart from ordinary phosphines: (1) the ether groups are labile but are not permanently lost from the coordination sphere; (2) complexes of these ligands exhibit unusual selectivity in a host of catalytic reactions including polymerization of ethene, carbonylation and hydrocarbonylation of methane, stereoselective hydrogenation, hydrosilylation and hydroformylation; and (3) ether substituents increase the electron density at the metal center thereby facilitating chemistry such as oxidative addition and reductive elimination.[13,14] Such attributes were noted long ago for these ligands, for example by Knowles and co-workers at Monsanto[13h], nevertheless it was not until the mid-1980's that ether–phosphine chemistry began to be broadly investigated by a number of groups, including our own.[13i–n,14] Highlights of some of our findings in this area are summarized later in this article.[14]

II. SOLVATED DINUCLEAR CATIONS

Synthetic Approaches to $[M_2(MeCN)_{10}]^{4+}$

Our main objective in undertaking an exploration of new acetonitrile chemistry is to access activated complexes for specific applications in coordination and materials chemistry. In expanding the class of homoleptic acetonitrile cations, we have targeted metals from the second and third row metals in low to intermediate oxidation states. An important back-drop for this chemistry is the work of Taube *et al.*, who demonstrated the existence of the aqueous metal–metal bonded cations $Mo_2(aq)^{4+}$ and $Rh_2(aq)^{4+}$.[15] Given the remarkable stability of these aqueous ions, we reasoned that it should be possible to prepare non-aqueous analogues. At the outset, we were aware of several promising reports by other research groups that lent credence to this premise. In 1983, Abbott *et al.* described the synthesis of $[Mo_2(NCCH_3)_8]^{4+}$ from reactions of $Mo_2(O_2CCH_3)_4$ with trifluoromethanesulfonic acid, but unfortunately efforts to fully characterize the Mo_2^{4+} species were hampered by difficulties encountered in isolating the compound from neat acid.[8] Several years later, the research groups of Cotton and Garner simultaneously reported a key result in this context, *viz.*, the reaction of $Mo_2(O_2CCH_3)_4$ with $R_3O^+BF_4^-$ (R = Me, Et) reagents in the presence of donor solvents. This chemistry produces the good leaving groups CH_3COOR and R_2O and the partially solvated dinuclear cations $[Mo_2(O_2CCH_3)_2(L)_6]^{2+}$ (L = MeCN, py).[16,17] Garner's group also reported identical results with Rh, thereby supporting the general nature of the approach.

A. Rhodium (II)

It occurred to us that, under forcing conditions, the chemistry leading to $[Rh_2(O_2CCH_3)_2(MeCN)_6]^{2+}$ would eventually result in complete substitution of the carboxylate groups. Indeed, the unbridged Rh_2(II,II) cation $[Rh_2(NCCH_3)_{10}]^{4+}$ was prepared in ~65% yield by simply heating the reaction of $Rh_2(OAc)_4(MeOH)_2$ with excess $[Et_3O][BF_4]$ in the presence of CH_3CN (Eq. (1)).[9a] Two additional methods were subsequently developed in our laboratories to synthesize the dinuclear cation in high yield (Eqs. (2) and (3)).[9b] Baranovskii and co-workers published the related molecule $[Rh_2(NCCH_3)_8(OH_2)_2]^{4+}$ from two entirely different routes involving the treatment of $Rh_2(O_2CCH_3)_4(MeOH)_2$ or $[Rh_2(SO_4)_4(H_2O)_2]^{4-}$ with HTFMS.[18]

$$\underset{\text{alkylation}}{\mathrm{Rh_2(O_2CCH_3)_4(MeOH)_2}} + \underset{1\underline{\mathrm{M}}\ \text{in}\ \mathrm{CH_2Cl_2}}{\mathrm{[Et_3O][BF_4]}} \xrightarrow[\text{10 days}]{\overset{\Delta}{\text{MeCN}}} \underset{\text{(55-65\% yield)}}{\mathrm{[Rh_2(MeCN)_{10}][BF_4]_4}} \tag{1}$$

$$\underset{\text{protonation}}{\mathrm{Rh_2(O_2CCH_3)_4(MeOH)_2}} + \mathrm{HBF_4 \cdot Et_2O} \xrightarrow[\text{7 days}]{\overset{\Delta}{\text{MeCN}}} \underset{\text{(60-70\% yield)}}{\mathrm{[Rh_2(MeCN)_{10}][BF_4]_4}} \tag{2}$$

$$\underset{\text{silyl esterification}}{\mathrm{Rh_2(O_2CCH_3)_4(MeOH)_2}} + \mathrm{Me_3Si(TFMS)} \xrightarrow[\text{7 days}]{\overset{\Delta}{\text{MeCN}}} \underset{\text{(65-75\% yield)}}{\mathrm{[Rh_2(MeCN)_{10}][TFMS]_4}} \tag{3}$$

The fact that acetonitrile cations of Rh_2^{4+} may be synthesized by at least five independent routes points to a remarkable stability for this unbridged dinuclear unit.

Characterization of the salt $[Rh_2(MeCN)_{10}][BF_4]_4$ by infrared and ^1H NMR spectroscopy, electrochemistry and X-ray crystallography revealed interesting behavior. The infrared spectrum shows the presence of coordinated CH_3CN ligands and BF_4^- groups, and ^1H NMR spectroscopy supports the fact that all ten nitrile ligands are substitutionally labile. Under anaerobic conditions, the ^1H NMR spectrum of a sample recrystallized in the dark consists of only one resonance at $\delta = +1.95$ ppm attributed to free CH_3CN. Electrochemical properties as determined by cyclic voltammetry reveal the existence of an irreversible reduction at $E_{p,c} = -0.05$ V vs. Ag/AgCl. The electronic absorption spectrum exhibits two characteristics feature at λ_{max}, nm (ϵ) = 468 (390 $M^{-1}cm^{-1}$) and 277 (22,000 $M^{-1}cm^{-1}$). In the course of attempting to collect a Raman spectrum on the compound, Woodruff and co-workers noted that the UV-visible spectrum of $[Rh_2(MeCN)_{10}]^{4+}$ was reversibly affected by the presence of light which was confirmed by detailed photochemical studies.[9d] Data indicate that $[Rh_2(MeCN)_{10}]^{4+}$ is dissociated into metastable photofragments of solvated Rh(II), Rh(I) and Rh(III) which eventually recombine to form the starting dinuclear complex in quantitative yield with a half-life of 1000 s. Interestingly, illumination with ambient room light ($\lambda_{max} < 600$ nm) is sufficient to effect photodissociation. A transient appearing in an irradiated sample of $[Rh_2^{II,II}(MeCN)_{10}]^{4+}$ at λ_{max} = 416 (15,000 $M^{-1}cm^{-1}$) is assigned to the $[Rh^I(MeCN)_4]^+$ photofragment. The presence of chlorinated solvents does not interfere with the reversibility of the reaction, which, along with other supporting data, suggests that redox rather than radical based chemistry dominates the photoreactivity of this system. One of the proposed intermediates in this chemistry is $[Rh^{I,II}(MeCN)_{10}]^{3+}$, which has been shown by electrochemistry to be an unstable molecule due to a chemical process that occurs between 0.1 and 1 s after reduction. Bulk electrolytic reduction of $[Rh_2^{II,II}(MeCN)_{10}][BF_4]_4$ results in quantitative production of an insoluble green-grey material at high ionic strengths of supporting electrolyte. Dissolution of the green-grey product in CH_3CN, which is the only solvent that dissolves the compound, results in the formation of a red-orange solution, the spectral properties of which correspond exactly to a mixture of $[Rh_2^{II,II}(MeCN)_{10}]^{4+}$ and the 416 nm species assigned to $[Rh(MeCN)_4]^+$. We take the results of this experiment as good evidence for the reduced "Rh(I)–Rh(II)" species being an unstable intermediate in the photochemical pathway that leads to the charge-separated $[Rh^{I}(MeCN)_4]^+$ and $[Rh^{III}(MeCN)_6]^{3+}$ cations. The mechanism initially involves homolytic Rh–Rh bond cleavage to produce Rh(II), a process that is also accessible thermally. Upon refluxing $[Rh_2(MeCN)_{10}][BF_4]_4$ in CH_3CN for 4 h, the electronic spectral properties match those of the irradiated sample. Moreover, the thermal "decomposition" process is also reversible.[19]

The crystal structure of $[Rh_2(MeCN)_{10}][BF_4]_4$ reveals an unbridged $[Rh_2]^{4+}$ unit in an octahedral arrangement consisting of five ligands with the sixth coordination site being occupied by the other metal (Fig. 2). The center of the Rh–Rh bond axis resides on a crystallographic C_2 axis. The equatorial planes of CH_3CN are twisted with respect to each other, as expected for a single bond, with an average torsion angle of $\chi = 44.8\ [2]°$. The axial CH_3CN

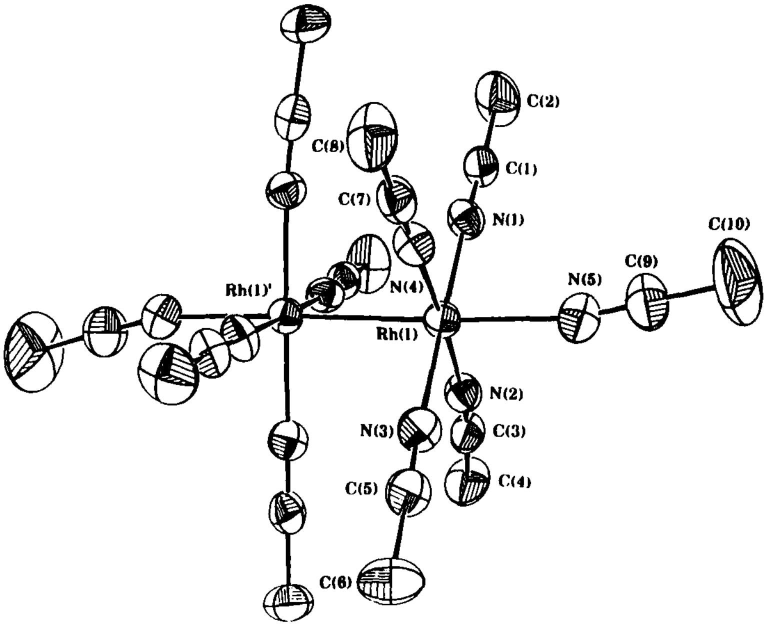
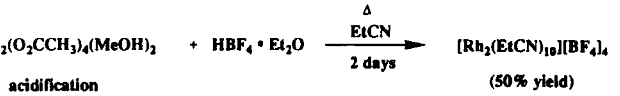


FIGURE 2 ORTEP diagram of the cation $[Rh_2(MeCN)_{10}]^{4+}$ with 40% probability ellipsoids.

groups deviate somewhat from linearity, which reduces the molecular symmetry from strictly D_{4d} to C_2. While this cation is not the first example of an unbridged Rh–Rh bond, it does represent a rare example of a Rh–Rh bond in the absence of any significant steric repulsion. The Rh–Rh distance of 2.64 (1) Å is longer than most other Rh(II,II) complexes with bridging groups (2.35–2.45 Å) but much shorter than those found in the unbridged complexes $Rh_2(dmg)_4(PPh_3)_2$ (2.936 (2) Å)[20] and $[Rh_2(p\text{-}CH_3C_6H_4NC)_8I_2]^{2+}$ (2.785 (2) Å).[21] In the dmg compound, the equatorial ligands are close to achieving the maximum torsion angle, but the added presence of bulky axial PPh_3 groups prevents the ligands from further relieving steric repulsion by bending away from each other.

A. (i) Solution Behavior of $[Rh_2(MeCN)_{10}][X]_4$ ($X = BF_4^-, CF_3SO_3^-$)

For a molecule as fundamentally simple as $[Rh_2(MeCN)_{10}]^{4+}$, it is important to establish elementary reactivity trends. To this end, we have investigated various exchange reactions of the CH_3CN ligands with a variety of donors and the reverse reactions to the tetraacetate starting material. We quickly discovered that the $[BF_4]^-$ salt is fairly insoluble in all solvents except CH_3CN and CH_3NO_2, although, curiously, clean axial exchange reactions occur without dissolution of the compound if the solid is placed in contact with a donor solvent such as ketones, alcohols or ethers. This is evidenced by dramatic color changes and by the disappearance of one band in the $\nu(C{\equiv}N)$ region of the infrared spectrum. Unfortunately, complete substitution of the CH_3CN groups in $[Rh_2(MeCN)_{10}][BF_4]_4$ under non-aqueous conditions is complicated by solubility problems; for example one can not even prepare the corresponding cations with propionitrile or benzonitrile ligands by this method. Furthermore, metathetic exchange of the BF_4^- anions with PF_6^-, $CF_3SO_3^-$ and BPh_4^- leads to separation problems, effectively ruling out the convenient preparation of other salts starting from the BF_4^- salt. We have circumvented these problems by preparing new analogues such as the $CF_3SO_3^-$ salts of acetonitrile or propionitrile cations from reactions of $Rh_2(OAc)_4(MeOH)_2$ with $Me_3Si(CF_3SO_3)$ in the presence of RCN (R = Me, Et). The propionitrile derivative can also be synthesized in high yield from tetrafluoroboric acid as depicted in Eq. (4).



$$\underset{\text{acidification}}{Rh_2(O_2CCH_3)_4(MeOH)_2} + HBF_4 \cdot Et_2O \xrightarrow[\text{2 days}]{\overset{\Delta}{EtCN}} \underset{\text{(50\% yield)}}{[Rh_2(EtCN)_{10}][BF_4]_4} \tag{4}$$

Substitution chemistry of $[Rh_2(MeCN)_{10}]^{4+}$ may proceed with retention or disruption of the Rh–Rh bond depending on the nature of the incoming ligand; in the latter case we have taken advantage of the non-redox nature of the reaction to prepare mononuclear Rh(II) complexes in high yield with ether–phosphine ligands (vide infra).[14a] Clearly, the absence of the bridging ligands in the complex $[Rh_2(MeCN)_{10}]^{4+}$ promises to enable the access of many new compounds not easily obtained by more conventional routes such as via replacement of acetate groups in $Rh_2(OAc)_4$. Chemistry of this nature will be discussed in the section involving the bulky ether–phosphine reactions.

A. (ii) Synthesis of $Rh_2(aq)^{n+}$

A series of color changes from orange through purple to green ensue when the cation $[Rh_2(MeCN)_{10}]^{4+}$ is dissolved and heated in H_2O under anaerobic conditions. These changes reflect the increasing ratio of oxygen donor ligands to nitrogen donors that are present in the Rh_2^{4+} coordination sphere as partially substituted $Rh_2(MeCN)_{10-x}(OH_2)_x]^{n+}$ complexes are formed. The reaction is slow, but is facilitated by the higher boiling point of water. The liberated CH_3CN is removed from the system by pumping, thus shifting the equilibrium towards the water substituted products. Eventually, an air-stable green solid is obtained by pumping the solution to dryness. This method of preparation is much more convenient than the procedure reported twenty-five years ago by Maspero and Taube in which a solution of the dirhodium aqua species $[Rh_2(aq)]^{4+}$ was produced via reduction of $[Rh(H_2O)_5Cl]^{2+}$ with $[Cr(H_2O)_6]^{2+}$ and purified on a Dowex exchange column by elution with $3M$ $HClO_4$.[15] The authors based their formulation of the product as a dinuclear $Rh_2^{II,II}$ on solution spectroscopic and magnetic properties as well as by its ion exchange behavior. The green solid isolated from the water reaction chemistry of $[Rh_2(MeCN)_{10}]^{4+}$ was subjected to several methods of characterization. Infrared spectral properties show prominent $\nu(OH)$ bands at 3445 and 3213 as well as $\delta(OH)$ modes at 1661 and 1597 cm^{-1}.

TABLE I

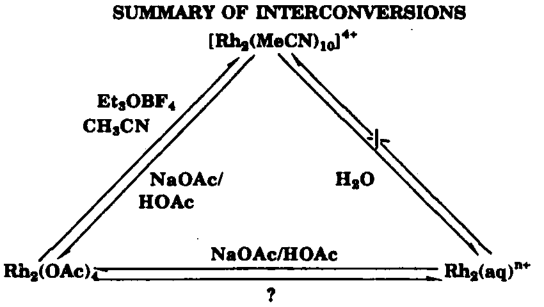
Comparison of visible spectra and reactivity for $Rh_2^{II,II}(aq)^{n+}$.

	Synthesized from $[Rh_2(MeCN)_{10}]^{4+}$	Synthesized from $[Rh(H_2O)_5Cl]^{2+}$ and Cr^{2+}
λ_{max} in H_2O	587 nm	[a]
λ_{max} in 3M $HClO_4$	600 nm[b] 580 nm[c]	648 or 630 nm
Converts back to $Rh_2(OAc)_4$ in CH_3COOH	yes	yes

[a] A value was not reported in H_2O as the sample can not be isolated from 3M $HClO_4$.

[b] Sample was prepared in H_2O.

[c] Sample was prepared in 3M $HClO_4$.



SCHEME 1 Interconversions of $Rh_2(aq)^{4+}$, $Rh_2(OAc)_4$ and $[Rh_2(MeCN)_{10}]^{4+}$.

The absence of $\nu(C{\equiv}N)$ stretches between 2200 and 2400 supports the conclusion that little if any coordinated CH_3CN remains. In an attempt to compare our results to those reported by Taube, we prepared three different samples of "$Rh_2(aq)^{4+}$" and examined their electronic properties. The results are summarized in Table I. The low energy visible band, assigned to $Rh{-}Rh\pi^* \rightarrow Rh{-}Rh\sigma^*$ in $Rh_2(O_2CR_3)_4L_2$ systems, shifts by as much as 20 nm from one preparative method to another in both our studies and in the earlier reports by Taube doubtless due to pH differences. What is most important, however, is that all samples easily revert back to $Rh_2(OAc)_4$ upon reaction with HOAc and NaOAc, thereby strongly supporting the existence of a remarkably stable Rh_2^{4+} core that remains intact under conditions of refluxing water and strong acid conditions. Scheme 1 depicts the interconversions demonstrated in our work that underscore the robust nature of the dirhodium unit.

B. Molybdenum (III)

Early after our discovery of the cation $[Rh_2(MeCN)_{10}]^{4+}$, we became interested in the feasibility of preparing examples with other metals. We had already noted the work of Abbott *et al.* in preparing the quadruply-bonded cation $[Mo_2(MeCN)_{10}]^{4+}$ [8a,6] and knew of similar chemistry going on in Cotton's laboratories.[8c,d] There were no reports, however, of a homoleptic acetonitrile cation for the Mo(III) oxidation state. We reasoned that excellent precursors to such a species would be partially solvated Mo(III) halides such as $MoCl_3(THF)_3$, and, indeed, reactions of $MoCl_3(THF)_3$ or $MoCl_3(MeCN)_3$ with 3 equivalents of $AgBF_4$ produce large quantities of AgCl and presumably the highly oxophilic solvated Mo(III) cation "$[Mo(MeCN)_6]^{3+}$." This species rapidly decomposes, however, with the deposition of Ag(s). The final isolated product is the salt $[Mo_2^{IV,IV}(\mu\text{-}F)(MeCN)_8O_2][BF_4]_3$ that contains a single bridging fluorine atom and two terminal oxo ligands.[22] Scheme 2 outlines a proposed pathway for the formation of this species that is based on collective findings from a variety of experiments. Figure 3 shows an ORTEP diagram of the cation. Salient points to note are the staggered arrangement of the two sets of equatorial nitrogen atoms (χ_{av} = 45.0°[2]) and the Mo–F–Mo angle of 165.0°. The latter is a primary indication of the degree of π-bonding between the fluorine and the metal atoms; a linear bridge signifies extensive π-bonding whereas an angle of 165° connotes much less

$$\text{(1)}\quad \mathrm{Mo^{III}Cl_3(NCCH_3)_3 + 3AgBF_4 \longrightarrow [Mo^{III}(NCCH_3)_6][BF_4]_3 + 3AgCl}$$

$$\text{(2)}\quad \mathrm{[Mo^{III}(NCCH_3)_6]^{3+} + Ag^{I} \longrightarrow [Mo^{IV}(NCCH_3)_6]^{4+} + Ag^{0}}$$

$$\text{(3)}\quad \mathrm{[Mo^{IV}(NCCH_3)_6]^{4+} + [O] \longrightarrow [O{=}Mo^{IV}(NCCH_3)_5]^{2+}}$$

$$\mathrm{([O] = THF\ or\ H_2O)}$$

$$\text{(4)}\quad \mathrm{2[O{=}Mo^{IV}(NCCH_3)_5]^{2+} + F^{-} \longrightarrow [\{O{=}Mo^{IV}(NCCH_3)_4\}_2(\mu\text{-}F)]^{3+}}$$

SCHEME 2 Postulated pathway for formation of $[Mo_2(\mu\text{-}F)(MeCN)_8O_2]^{3+}$.

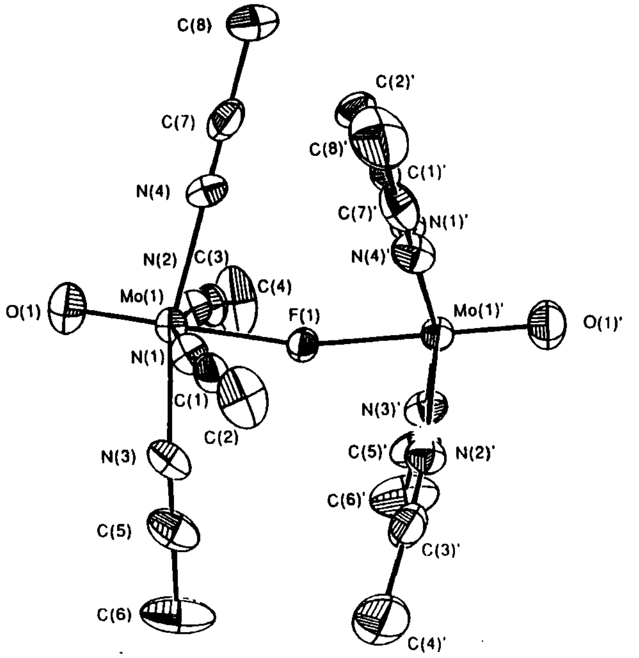


FIGURE 3 ORTEP diagram of $[Mo_2(\mu\text{-}F)(MeCN)_8O_2]^{3+}$ with 40% probability ellipsoids.

π-character. The cation $[Mo_2(\mu\text{-}F)(MeCN)_8O_2]^{3+}$ contains eight dissociable solvent ligands, is highly substitutionally labile and therefore potentially quite useful for high oxidation state non-aqueous molybdenum chemistry. This example is the first of its kind based on the arrangement $[O{=}Mo^{IV}{-}F{-}Mo^{IV}{=}O]^{3+}$.

C. Rhenium(II)

It is a well-established principle that, in general, the chemistry of first row transition metals does not translate well to the heavier elements.[1] Nevertheless, we have found that simple protonation reactions of dinuclear rhenium halides proceed to give solvated cations much like the classical reactions of 3d metals.[4] This chemistry has resulted in the isolation and full characterization of the first example of a triply-bonded solvated cation, namely $[Re_2(MeCN)_{10}]^{4+}$.[9c] Three different Re starting materials have been employed (Eqs. (5)–(7)), with several additional methods also yielding promising results. Of the three reactions outlined below, only Eq. (7) is an extrapolation of known chemistry of Mo_2(II,II) and Rh_2(II,II). Equations (5) and (6), entirely without precedence in metal–metal bond chemistry, are actually quite remarkable. One method begins with the seminal quadruply-bonded compound $[Re_2Cl_8]^{2-}$ and the other with the generally unreactive triply-bonded phosphine complexes of the type $Re_2Cl_4(PR_3)_4$.[23]

$$[(C_4H_9)_4N]_2[Re_2^{III,III}Cl_8] \xrightarrow[\substack{\text{heat}\\ \text{5 hr}}]{\substack{\text{xs } HBF_4\cdot Et_2O\\ CH_3CN/CH_2Cl_2}} \underset{\text{blue crystalline solid (~ 15\% yield)}}{[Re_2^{II,II}(MeCN)_{10}][BF_4]_4} \quad (5)$$

$$\searrow HCl\uparrow + \boxed{\text{other products}}$$

$$Re_2^{II,II}Cl_4(P^nPr_3)_4 \xrightarrow[\substack{\text{heat}\\ CH_2Cl_2}]{\text{xs } HBF_4\cdot Et_2O,\ CH_3CN} \underset{\text{(~ 70\% yield)}}{[Re_2^{II,II}(MeCN)_{10}][BF_4]_4} \quad (6)$$

$$\searrow HCl\uparrow + HP^nPr_3$$

$$Re_2(O_2CC_3H_7)_4Cl_2 + 2AgBF_4 \xrightarrow{CH_3CN} [Re_2(O_2CC_3H_7)_4(MeCN)_2][BF_4]_2 \quad (7a)$$

$$\searrow AgCl\downarrow$$

$$[Re_2^{III,III}(O_2CC_3H_7)_4(MeCN)_2][BF_4]_2 \xrightarrow[\substack{CH_3CN\\ \Delta,\ \text{18 days}}]{Et_3OBF_4} \xrightarrow[0^\circ C]{CH_2Cl_2} \underset{\text{(~ 40\% yield)}}{[Re_2^{II,II}(MeCN)_{10}][BF_4]_4} \quad (7b)$$

These reactions hint at a great deal of unexplored chemistry of metal halides and phosphine complexes of the second and third row transition metals. Efforts to generalize this approach to other metals are underway and appear to be quite promising.

IR spectra of $[Re_2(MeCN)_{10}][BF_4]_4$ exhibit absorptions assigned to coordinated CH_3CN and $[BF_4]^-$. A ^1H NMR spectrum in CD_3CN exhibits a resonance at $\delta = +3.37$ ppm attributed to the equatorially bound CH_3CN groups and a minor feature at $\delta = +1.95$ due to free CH_3CN. The electronic properties of $[Re_2(MeCN)_{10}][BF_4]_4$ in the visible region consist of a very broad low energy transition at $\lambda_{max}(nm) = 663$ ($\epsilon = 630\ M^{-1}cm^{-1}$) in addition to a strong feature of nearly equal intensity at 593 ($\epsilon = 591\ M^{-1}cm^{-1}$) with two shoulders located at 458 and 866. Bands in the UV region occur at 244 ($\epsilon = 2.7 \times 10^4\ M^{-1}cm^{-1}$) and 203 ($\epsilon = 5.1 \times 10^4\ M^{-1}cm^{-1}$). Electrochemical measurements revealed, surprisingly, a quasi-reversible reduction at $E_{1/2} = +0.24$ V along with two irreversible reductions at $E_{p,c} = -0.20$ V and -0.76 V vs. Ag/AgCl. Ordinarily, compounds with a Re_2^{4+} core ($\sigma^2\pi^4\delta^2\delta^{*2}$) exhibit two, usually reversible, one-electron oxidations corresponding to sequential loss of electrons from the δ^* orbital. Clearly the relative HOMO/LUMO energies for the new solvated Re_2^{4+} species are unlike those found for the classical Re≡Re molecules; detailed spectral and theoretical studies are required in order to fully understand its properties.

C. (i) Structural Determination of $[Re_2(MeCN)_{10}][Mo_6O_{19}]_2$

Single crystals of $[Re_2(MeCN)_{10}][BF_4]_4$ isolated from the Et_3OBF_4 reaction in Eq. (7) were examined by X-ray crystallography and found to belong to a body-centered cubic space group in which the Re_2 units exhibit a three-fold disorder. Poor crystal quality coupled with considerable refinement difficulties prompted us to resort to an unusual strategy to reduce the crystal symmetry and improve packing, namely we replaced the small tetrahedral $[BF_4]^-$ counterions with large octahedral $[Mo_6O_{19}]^{2-}$ polyoxometallate anions. This leads to a perfectly ordered array of dimetal cations within the interstices provided by the large anions. The salt $[Re_2(MeCN)_{10}][Mo_6O_{19}]_2$ was prepared by an exchange reaction of $[Re_2(MeCN)_{10}][BF_4]_4$ and $[(n\text{-}C_4H_9)_4N]_2[Mo_6O_{19}]$ in CH_3CN (Eq. (8)).

$$[Re_2(NCCH_3)_{10}][BF_4]_4 + 2[Bu_4N]_2[Mo_6O_{19}] \xrightarrow{CH_3CN} \underset{(\sim 70\%\ \text{yield})}{[Re_2(NCCH_3)_{10}][Mo_6O_{19}]_2} \quad (8)$$

An IR spectrum of the crystals confirmed that the $[BF_4]^-$ had been replaced by the $[Mo_6O_{19}]^{2-}$ counterion without degradation of the original cation. A single crystal X-ray data confirmed the identity of the new compound as $[Re_2(MeCN)_{10}][Mo_6O_{19}]_2$ with a 1:2 cation:anion ratio, indicating that a reduction of the parent complex occurs in the reaction pathway when starting from $[Re_2Cl_8]^{2-}$ or $Re_2(C_3H_7COO)_4Cl_2$. ORTEP plots of the three constituent ions in $[Re_2(MeCN)_{10}][Mo_6O_{19}]_2$ are depicted in Fig. 4. The molecule crystallizes in the monoclinic space group C2/c with the midpoint

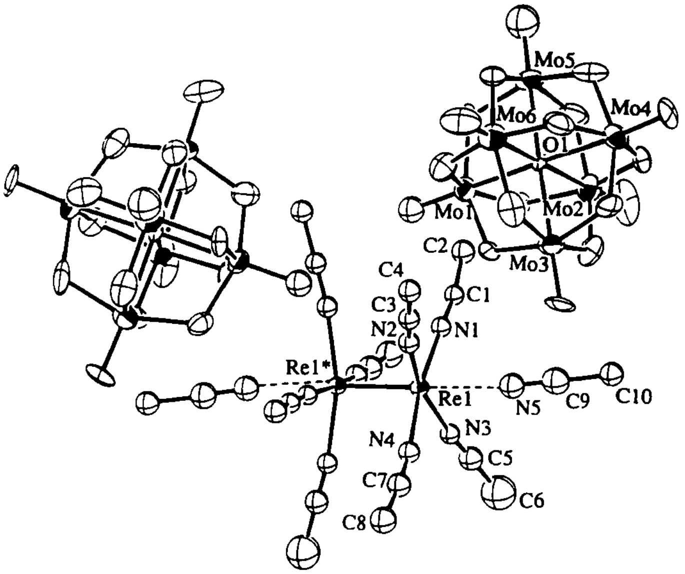
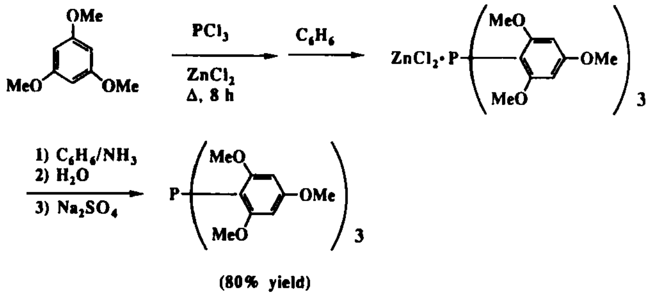


FIGURE 4 ORTEP of the constituent ions in the salt $[Re_2(MeCN)_{10}][Mo_6O_{19}]_2$ with 40% probability ellipsoids.

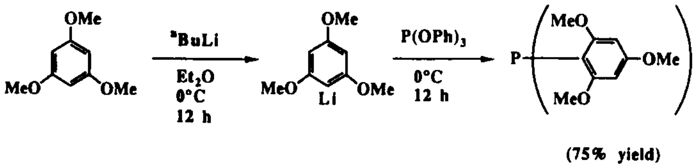
of the Re–Re bond residing on a two-fold symmetry axis. The environment of each Re(II) center is pseudo-octahedral, consisting of four nearly planar CH_3CN ligands and two additional vertices defined by a weakly interacting axial CH_3CN group (Re–N = 2.51 (3) Å) and the other Re atom. Unlike the eclipsed quadruply-bonded cation $[Mo_2]^{4+}$, the dirhenium molecule adopts a staggered conformation in which the two $Re(NCCH_3)_4$ units are rotated by χ_{av} = 44.5 [1]°. The Re–Re distance of 2.259 (4) Å falls in the range observed for dirhenium compounds containing metal–metal triple bonds of the electron rich $\sigma^2\pi^4\delta^2\delta^{*2}$ configuration, despite the fact that the metal centers are highly charged and are not supported by strong σ or π donors such as phosphine or halide ligands.

III. STABILIZATION OF d^7 METAL SYSTEMS WITH AN ETHER–PHOSPHINE LIGAND

We have been investigating a non-commercially available ether–phosphine that appeared in the Soviet literature in 1959, but which has gone virtually unexplored in transition metal chemistry since that time.[24a–c] The phosphine, tris(2,4,6-trimethoxyphenyl)phosphine, which we refer to as TMPP, resurfaced in 1984 in the laboratories of Wada and co-workers who reported its synthesis by a different route.[24d] Since their initial communication, this group has shown TMPP to be a remarkably useful reagent for mild ring-opening reactions of terminal epoxides and facile dealkylation reactions.[24e–g] We have adapted both preparations of TMPP in our laboratories and found the conditions outlined in Eqs. (9) and (10) to be ideal. The syntheses are straightforward and the compound is an air and thermally stable solid.



(9)



(10)

In considering the potential chemistry of TMPP, it is instructive to place its properties in perspective to those observed for other common phosphines.[25] The presence of methoxy substituents renders the phosphine both very bulky and basic in addition to providing numerous coordination sides for metal binding. Furthermore, the combination of "hard" and "soft" donors adds versatility and allows the ligand to stabilize metals in a variety of oxidation states. We carried out a crystal structure to determine the cone angle of the free ligand and to observe the orientation of the methoxy groups with respect to the rings. The ORTEP plot in Fig. 5 clearly reveals the familiar pinwheel arrangement of phenyl substituents with all $-OCH_3$ groups lying in the plane of the ring. To determine the electron donating capability of TMPP, we synthe-

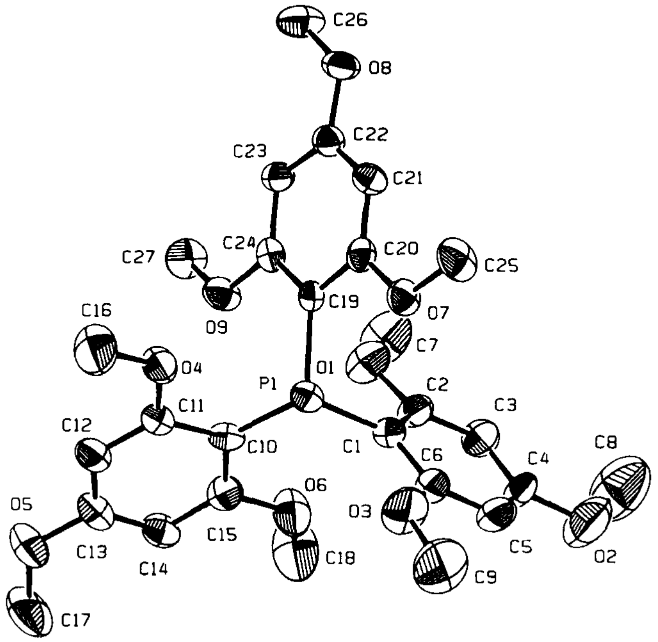


FIGURE 5 ORTEP representation of a molecule of the phosphine tris(2,4,6-trimethoxyphenyl)phosphine (TMPP) with 40% probability ellipsoids.

sized $Ni(CO)_3(TMPP)$ and measured its infrared spectrum. A plot of $\nu_{A1}(CO)$ versus cone angle is depicted in Fig. 6. The Tolman cone angle for TMPP is 184°, which places it third on the scale of size behind $P(o\text{-tolyl})_3$ and $P(mesityl)_3$ (Fig. 7).

Work in our laboratories over the past several years points to a rich coordination, organometallic and electron-transfer chemistry for metal centers supported by tris(2,4,6-trimethoxyphenyl)phosphine.[14] A number of potential applications for these phosphine complexes have emerged from our research. We shall limit our discussion in this paper to the chemistry of TMPP with solvated homoleptic acetonitrile precursors, the aim of which is to produce cationic d^7 homoleptic phosphine products. Apart from Co(II) and to a lesser degree Ni(III), little is known regarding the chemistry of d^7 metal ions, primarily since these species are highly reactive, appearing mainly as short-lived intermediates or impurities in the chemistry of d^6 and d^8 metal complexes. It is of considerable in-

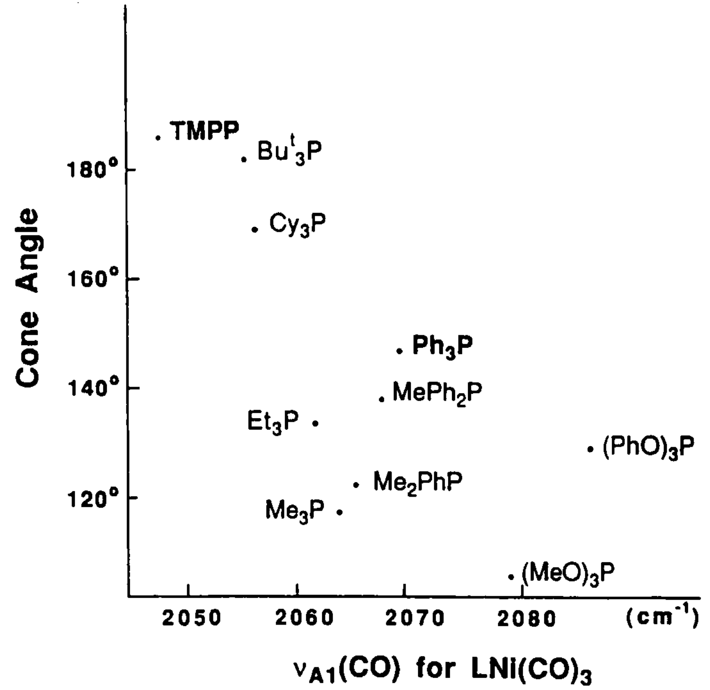


FIGURE 6 Plot of ν_{A1}(CO) versus cone angle for a group of phosphines including TMPP. The values for the other phosphines were reported by Tolman in Ref. 48(a); a similar plot minus TMPP was depicted in Ref. 48[b].

terest to design d^7 complexes and study their reactivity in stoichiometric and catalytic reactions of the late transition elements, especially Rh, in which their presence has been detected but whose potential role in the chemistry is not known.[26,27f] Metalloradicals exhibit promise for undergoing reversible reactions with small molecules such as CO and O_2 since they often bind more weakly to these substrates than their d^8 counterparts. For these reasons and for the general purpose of delineating reaction pathways for elusive metalloradicals, we have been engaged in efforts to design mononuclear d^7 complexes of the second and third row transition metals; our goal is to engender stability in the solid-state by using a bulky ligand that possesses pendent ether groups that are capable of coordinating in the solid state but which are easily displaced in solution.

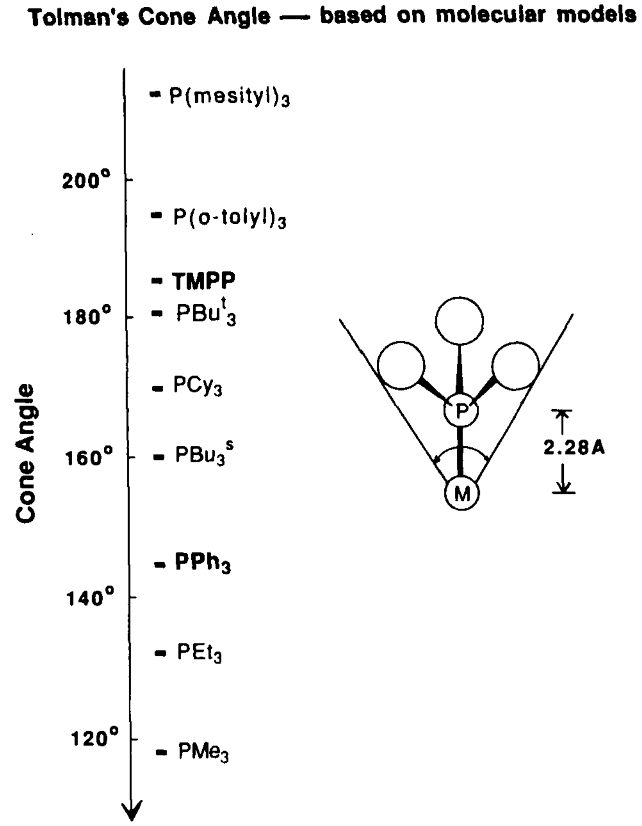


FIGURE 7 A graph depicting the cone angles for common phosphines. The Tolman cone angles for the ligands other than TMPP were taken from Ref. 48(a).

A. Chemistry of $[Rh_2(MeCN)_{10}]^{4+}$ with TMPP

A. (i) Synthesis of $[Rh(\eta^3\text{-TMPP})_2]^{2+}$

An excellent area of application for the TMPP ligand is the stabilization of mononuclear Rh(II) complexes. In contrast to the well-known Co(II) d^7 molecules, little is known about the structures or reactivity of the Rh(II) analogues.[27-29] Our research in the area of mononuclear Rh(II) phosphine chemistry, using the solvated dinuclear complex $[Rh_2(MeCN)_{10}]^{4+}$ as a starting material, produced the first example of a structurally characterized sixcoordinate Rh(II) complex without a metal–metal bond. The highly unusual mononuclear rhodium (II) complex, $[Rh(\eta^3\text{-TMPP})_2][BF_4]_2$ was isolated in high yield by the reaction shown below in Eq. (11).

$$[Rh_2(MeCN)_{10}][BF_4]_4 + 4\ \mathrm{TMPP} \xrightarrow[0^\circ C]{MeCN} \underset{\text{(yield 91\%)}}{[Rh(\eta^3\text{-TMPP})_2][BF_4]_2} \qquad (11)$$

The molecular cation, shown in Fig. 8, consists of two TMPP ligands bonded to the Rh atom in a face-capping mode through the oxygen atoms of two pendent methoxy-groups and the phos-

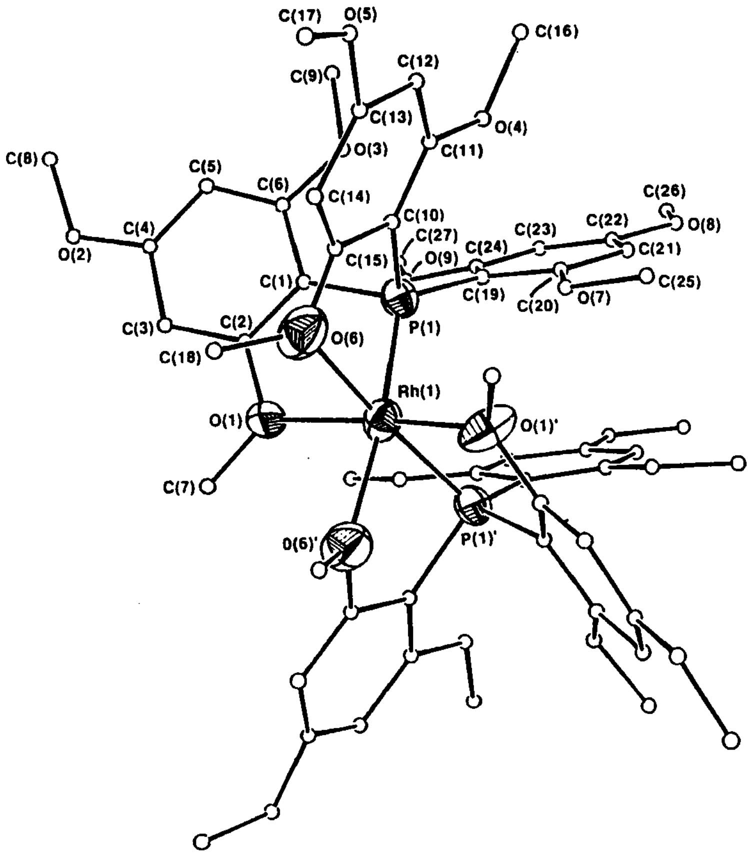


FIGURE 8 Molecular structure of the cation $[Rh(\eta^3\text{-TMPP})_2]^{2+}$ with 40% probability ellipsoids.

phorus atom. The most striking aspect of the structure is the fact that the phosphines lie cis to each other rather than in the trans arrangement that would be anticipated on the basis of steric arguments alone. There are two structurally distinct metal–ether interactions, with the oxygen atoms trans to phosphorus bonded at a distance of 2.201(6) Å and the mutually trans oxygen atoms at Rh–O distances of 2.398(1) Å. EPR measurements of [Rh(η^3-TMPP)$_2$][BF$_4$]$_2$ were carried out in a variety of solvents at r.t. and 77 K. Solutions in CH_2Cl_2, acetonitrile/toluene (1:1) and CH_2Cl_2/Me-THF (1:1) produced identical spectra at r.t. with a single isotropic homogeneous line at $g \approx 2.20$. At 77 K in the solvent mixtures, which form glasses at this temperature, a rhombic signal was observed (Fig. 9). The g-values of the CH_2Cl_2/MeTHF system are $g_{xx} = 2.25$, $g_{yy} = 2.30$ and $g_{zz} = 1.99$. The average of the three anisotropic g-values equals that of the isotropic line at r.t.; therefore the change in lineshape is due to the rapid tumbling of the complex in solution, as opposed to being frozen in random orientations with respect to the applied field at 77 K. In the anisotropic spectrum (77K), g_{zz} is split into a doublet due to the hyperfine interaction with the $I = 1/2$ nucleus of Rh.

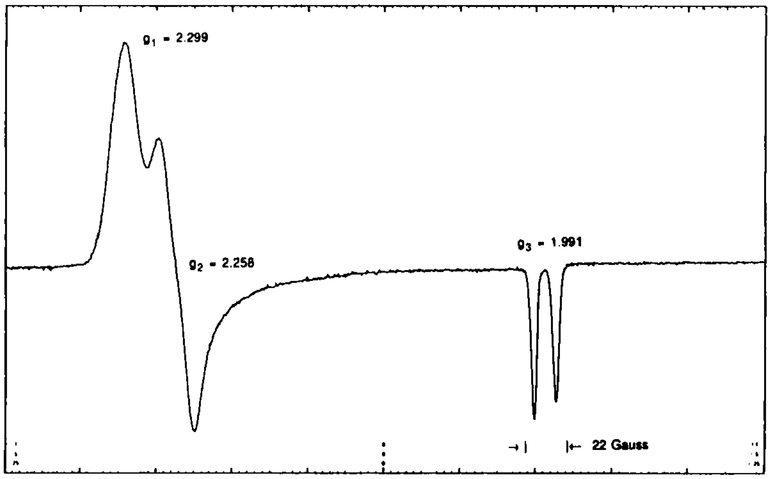
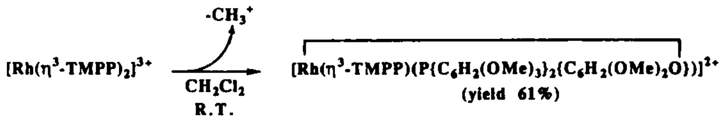


FIGURE 9 X-band EPR spectrum of [Rh(η^3-TMPP)$_2$]$^{2+}$ in Me–THF at 77 K indicating the three g values. The $A_\parallel$ of 22 Gauss is due to ^{103}Rh ($I = 1/2$).

A. (ii) Properties of $[Rh(\eta^3\text{-}TMPP)_2]^{2+}$

The compound $[Rh(\eta^3\text{-}TMPP)_2][BF_4]_2$ is soluble in methylene chloride and acetonitrile, partially soluble in methanol and chloroform, and completely insoluble in water, tetrahydrofuran, diethylether and hydrocarbon solvents. The complex is remarkably air-stable, with solid samples being indefinitely stable, and CH_2Cl_2 solutions decomposing only after several weeks in air. These observations are somewhat surprising considering the documented, sensitive nature of mononuclear Rh(II) complexes.[27,28] In spite of its rather inert behavior towards oxygen and chlorinated solvents, the cation nonetheless exhibits rich redox behavior. Chemical or electrochemical oxidation produces the d^6 complex $[Rh(\eta^3\text{-}TMPP)_2][BF_4]_3$ with a ligand arrangement identical to that found in the parent complex. In striking contrast to the stability of the divalent complex $[Rh(\eta^3\text{-}TMPP)_2][BF_4]_2$, this Rh(III) species is air-sensitive and thermally unstable, rapidly converting to the demethylated Rh(III) complex, $[Rh(\eta^3\text{-}TMPP)(P\{C_6H_2(OMe)_2O\}\{C_6H_2(OMe)_3\}_2)][BF_4]_2$ at room temperature in a wide variety of solvents (Eq. (12)).



$$[Rh(\eta^3\text{-}TMPP)_2]^{3+} \xrightarrow[\substack{CH_2Cl_2 \\ R.T.}]{-CH_3^+} [Rh(\eta^3\text{-}TMPP)(P\{C_6H_2(OMe)_3\}_2\{C_6H_2(OMe)_2O\})]^{2+} \quad \text{(yield 61\%)} \qquad (12)$$

A. (iii) Carbon Monoxide Reactions

Few reports have addressed the reactivity of mononuclear Rh(II) complexes.[29] In light of recent reports by Wayland and co-workers of CO coupling and CH_4 activation at Rh(II) radical centers, this is a particularly attractive area of research.[30] $[Rh(\eta^3\text{-}TMPP)_2][BF_4]_2$ reacts with carbon monoxide at ambient temperatures and pressures to form an unstable $Rh(II)(CO)_2\cdot$ adduct that triggers a series of electron transfer reactions involving formation of two Rh(I) carbonyl complexes, $[Rh(TMPP)_2(CO)_2][BF_4]$ (Fig. 10) and $[Rh(\eta^2\text{-}TMPP)(TMPP)CO][BF_4]$ (Fig. 11) in addition to the Rh(III) complex $[Rh(\eta^3\text{-}TMPP)_2]^{3+}$. Upon purging the reaction solution with an inert gas, the original Rh(II) species is regenerated in quantitative yields. Intrigued by this reversible binding of CO to a radical

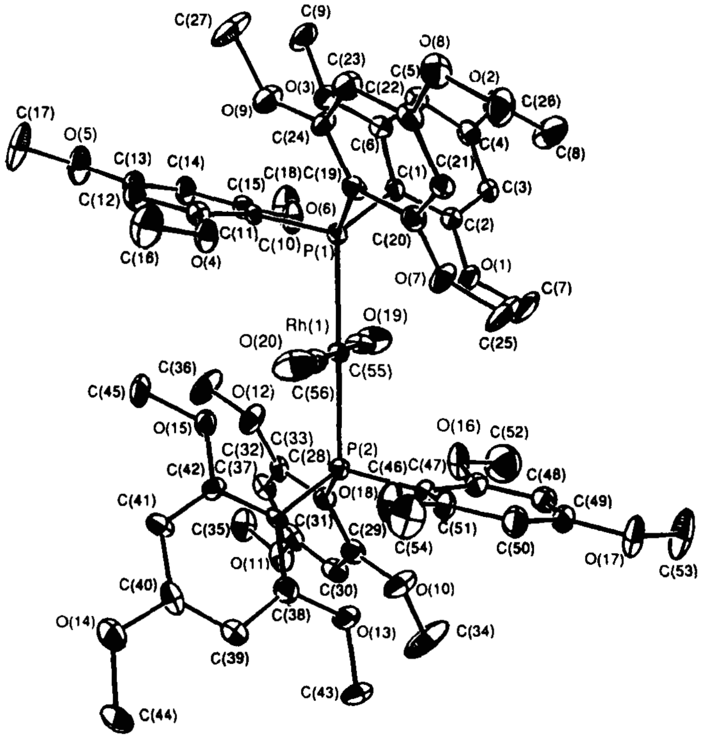


FIGURE 10 Molecular structure of the square planar dicarbonyl cation $[Rh(TMPP)_2(CO)_2]^+$.

d^7 metal complex, we undertook a variety of experiments, including labeling studies with ^{13}CO, to elucidate the pathway depicted in Scheme 3. Independent verification of the proposed reactions was obtained by designing independent synthetic routes to all of the stable intermediates and subsequently investigating their individual redox behavior and reactivity with carbon monoxide. Ultimately, we hope to understand the influence of steric versus electronic effects in dictating the reversibility of key reactions with metal–TMPP complexes in order to take advantage of the flexibility of the phosphine for useful stoichiometric or catalytic transformations of substrates. To this end, we have extended our chemistry of π-acceptor reactions to include various isocyanide ligands with widely different steric properties.

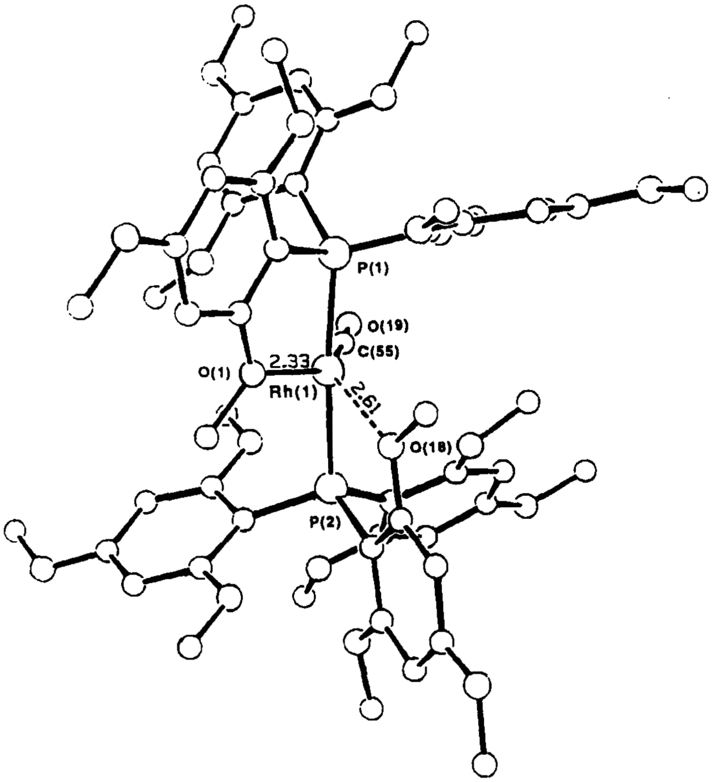
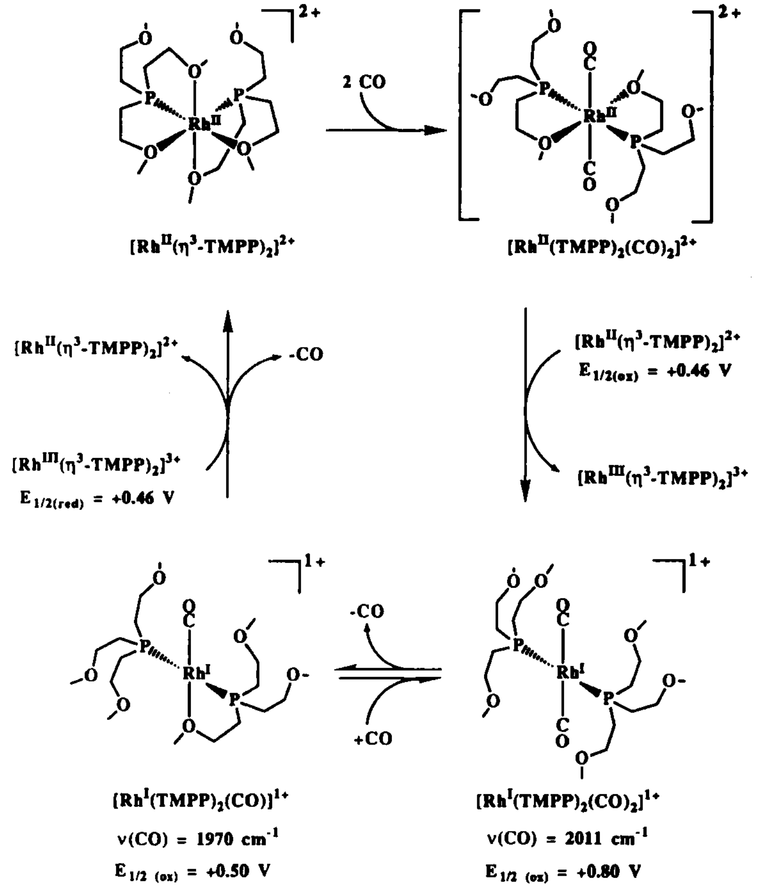


FIGURE 11 Molecular structure of $[Rh(\eta^2\text{-TMPP})(TMPP)(CO)]^+$ emphasizing the central coordination sphere of the metal and the pseudo-tbp geometry with a long ether interaction (---) occupying the fifth coordination site.

A. (iv) Isocyanide Reactions

Carbon monoxide adducts of $[Rh(\eta^3\text{-TMPP})_2]^{2+}$ are not stable, but quite different results are obtained with isocyanide ligands, the chemistry of which is subject to both steric and electronic control. In the cases where R = Pr^i and Bu^t, it is possible to isolate and structurally characterize the paramagnetic bis-isocyanide products of general formula $[Rh(CNR)_2(TMPP)_2][BF_4]_2$ (Eq. (13)).

$$[Rh(\eta^3\text{-TMPP})_2]^{2+} + 2\ CNBu^t \xrightarrow[R.T.]{CH_2Cl_2} \underset{\text{(yield 90\%)}}{[Rh(TMPP)_2(CNBu^t)_2]^{2+}} \qquad (13)$$



SCHEME 3 Proposed pathway for the reversible reaction between $[Rh(\eta^3\text{-TMPP})_2]^{2+}$ and CO.

A cyclic voltammogram of $[Rh(TMPP)_2(CNBu^t)_2][BF_4]_2$ in 0.1M $TBABF_4$–CH_2Cl_2 shows a reversible couple at $E_{1/2} = -0.04$ V vs. Ag/AgCl, corresponding to a one-electron reduction to Rh(I). Not surprisingly, this process is shifted to more positive potentials relative to that of $[Rh(\eta^3\text{-TMPP})_2][BF_4]_2$, due to the electron-withdrawing effect of the π-acceptor ligands. The Rh(II)/Rh(I) couple falls at a potential less positive than the Rh(II)/Rh(III) couple for the parent complex, $[Rh(\eta^3\text{-TMPP})_2]^{2+}$, and as a result, $[Rh(TMPP)_2(CNBu^t)_2]^{2+}$ is stable with respect to spontaneous reduction to Rh(I) in the presence of $[Rh(\eta^3\text{-TMPP})_2]^{2+}$. This is in sharp contrast to the situation in the analogous $[Rh(\eta^3\text{-TMPP})_2]^{2+}$/carbon monoxide chemistry. Besides providing the very first examples of stable π-acceptor complexes of divalent rhodium, this work supports our contention that a $Rh(II)(CO)_2\cdot$ intermediate is formed early in the carbon monoxide chemistry. An ORTEP drawing of the molecular cation $[Rh(TMPP)_2(CNBu^t)_2]^{2+}$ is shown in Fig. 12. The cation contains mutually trans phosphine and isocyanide ligands arranged in a slightly distorted square plane, as evidenced by the angles C(55)–Rh(I)–C(60) = 179.0 (3)° and

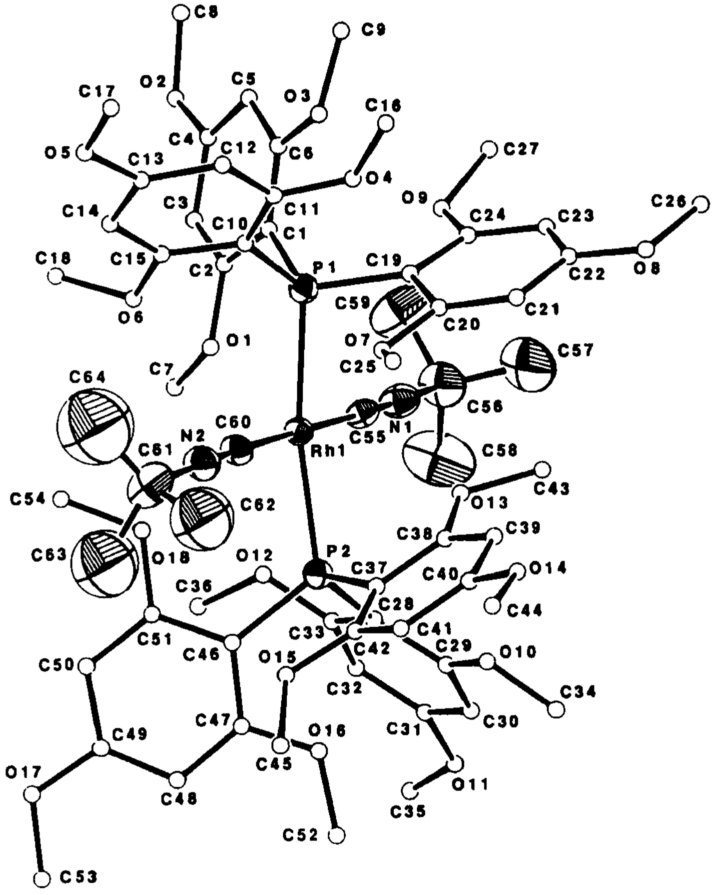


FIGURE 12 ORTEP representation of the cation $[Rh(TMPP)_2(CNBu^t)_2]^{2+}$.

P(1)–Rh(1)–P(2) = 168.78 (8)°. Unlike $[Rh(\eta^3\text{-TMPP})_2][BF_4]_2$ in which the rhodium atom is pseudo-octahedral with two metal–phosphorus and four metal–ether interactions, the title compound is bound to TMPP only through the phosphorus lone pair, leading to a four-coordinate geometry. The shortest Rh–O distances along the axial direction are Rh(1)–O(1) = 2.851 (5) Å and Rh(1)–O(13) = 2.909 (6) Å; these are well outside the expected range for covalent bonding. The trans Rh–P bond distances of 2.364 (2) Å and 2.380 (2) Å are longer than those found in the parent Rh(II) complex, and are indicative of the stronger trans effect exerted by the phosphine as compared to that of an ether donor. The paramagnetism of $[Rh(TMPP)_2(CNBu^t)_2][BF_4]_2$ was probed by several spectroscopic and magnetic techniques. The ^1H and ^{31}P NMR spectra of $[Rh(TMPP)_2(CNBu^t)_2][BF_4]_2$ are broad, consistent with the formulation of the compound as a paramagnetic species. The solid-state EPR spectrum of a polycrystalline sample at 100 K shows an axial signal with $g_\perp = 2.45$ and $g_\parallel = 1.96$ with hyperfine coupling to ^{103}Rh ($I = 1/2$) in the $g_\parallel$ region ($A_\parallel = 62$ G). The EPR spectrum in a 1:1 Me-THF/CH_2Cl_2 glass at 100 K (Fig. 13) exhibits a signal

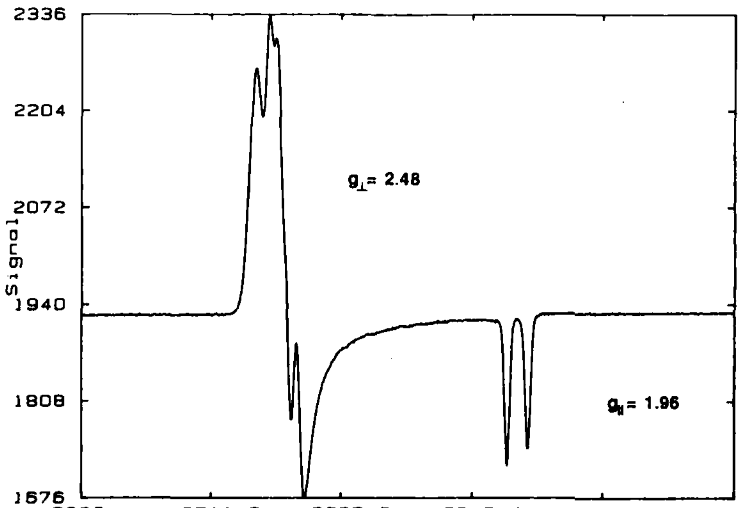


FIGURE 13 X-band EPR spectrum of $[Rh(TMPP)_2(CNBu^t)_2]^{2+}$ in a CH_2Cl_2/MeTHF glass at 100 K. The $A_\parallel$ hyperfine coupling to ^{103}Rh ($I = 1/2$) is 62 Gauss.

similar to that observed in the solid state ($g_\perp = 2.48$, $g_\parallel = 1.96$, $A_\parallel = 66$ G) with the exception that the $g_\perp$ region shows hyperfine coupling as well. A solid state magnetic susceptibility measurement at 299 K led to a μ_{eff} value of 2.04 B.M. Solution susceptibility studies by the Evans method gave a μ_{eff} of 2.20 at 293 K.

The results for the bulky isocyanides are in sharp contrast to the MeNC chemistry which follows a reaction course similar to that of CO, i.e., with no detectable Rh(II)(CNMe)$_x$ adducts. From this, we conclude that while kinetic stabilization is probably an important factor in dictating the course of the reactions with π-acceptor ligands, the modulation of the electron density at the metal center (a factor that controls the accessibility of the Rh(II)/Rh(III) couple) is also a primary determinant. Curiously, although $[Rh(\eta^3\text{-TMPP})_2]^{2+}$ undergoes ether-group dissociation and subsequent cis to trans isomerization in favor of π-acceptors, it is unreactive towards donors such as O_2. This is evidently a consequence of the electronic environment of the metal rather than a steric effect, since identical behavior has been noted for ether–phosphine complexes in which the ligand is not particularly bulky.[13e]

B. Reactivity Studies of $[M(MeCN)_6]^{2+}$ (M = Co, Ni) with TMPP

B. (i) Chemistry of Co(II)

The chemistry of Co(II) is an important area of investigation, particularly with respect to O_2 binding and transport.[31] A major advantage of five-coordinate Co(II) is that its complexes typically exhibit a low-spin electronic configuration, with an $S = 1/2$ ground state, thereby providing the researcher with a convenient EPR probe for elucidating small molecule binding and electron distribution. Given the bulk of the TMPP ligand and its dual nature as both a hard and a soft ligand, we reasoned that unusual Co(II) compounds would result from such a ligand environment. In the course of investigating the chemistry of Co(II) acetonitrile salts of $AlCl_4^-$, $SbCl_6^-$ and BF_4^-, we found that the chemistry was very sensitive to choice of solvent and counterion as well as to the presence of excess phosphine. When the reactions are carried out in the presence of a chloride source and in protic solvents, various phosphonium salts of $[CoCl_4]^{2-}$ are isolated. The reaction of

$[Co(MeCN)_6]^{2+}$ with 4 equivalents of TMPP in acetone, however, yields the neutral complex Co(TMPP-*O*)$_2$, whose formulation is based on spectroscopy, magnetism and mass spectrometry (Eq. (14)). The acronym TMPP-*O* refers to the phosphino-phenoxide form of the ligand, $\{P[C_6H_2(OCH_3)_3]_2[C_6H_2(OCH_3)_2O]\}^-$, derived from demethylation of one o-OMe group. The chemistry of Co(TMPP-*O*)$_2$ with MCl_2 species to give $Cl_2MCo\{\mu\text{-}\eta^2\text{-}(TMPP\text{-}O)_2\}$ (M = Co, Mn) as shown in Eqs. (15) and (16) suggests that the original mononuclear Co(II) complex exhibits a cis square planar geometry (Fig. 14).

$$[Co(MeCN)_6][BF_4]_2 + 4\,TMPP \xrightarrow[\text{r.t., 24 h}]{\text{Acetone}} \underset{\text{(70\% yield)}}{Co(TMPP\text{-}O)_2} + 2\,[CH_3\text{-}TMPP][BF_4] \tag{14}$$

$$CoCl_2 + Co(TMPP\text{-}O)_2 \xrightarrow[\Delta,\ 5\ h]{\text{Acetone}} \underset{\text{(75\% yield)}}{Cl_2Co_2\{\mu\text{-}\eta^2\text{-}(TMPP\text{-}O)_2\}} \tag{15}$$

$$MnCl_2 + Co(TMPP\text{-}O)_2 \xrightarrow[\Delta,\ 24\ h]{\text{Acetone}} \underset{\text{(40\% yield)}}{Cl_2MnCo\{\mu\text{-}\eta^2\text{-}(TMPP\text{-}O)_2\}} \tag{16}$$

The formation of dinuclear complexes is an intriguing facet of the chemistry of TMPP-*O* complexes. As the ORTEP diagrams in Figs. 15 and 16 clearly show, the halide supported metals are tetrahedral whereas the Co(TMPP-*O*)$_2$ unit is square planar with cis P atoms and no axial interactions.

The molecule Co(TMPP-*O*)$_2$ is formally a 15-electron complex if axial ether interactions are absent, and would be expected to be

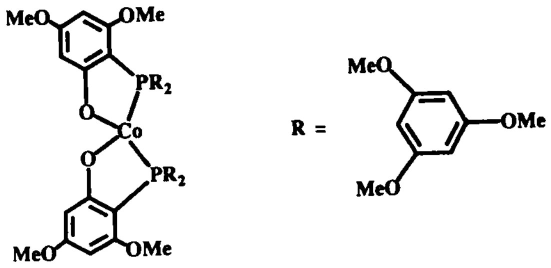


FIGURE 14 Proposed structure of Co(TMPP-*O*)$_2$ containing two chelating phosphine phenoxide ligands (TMPP-*O*) derived from TMPP.

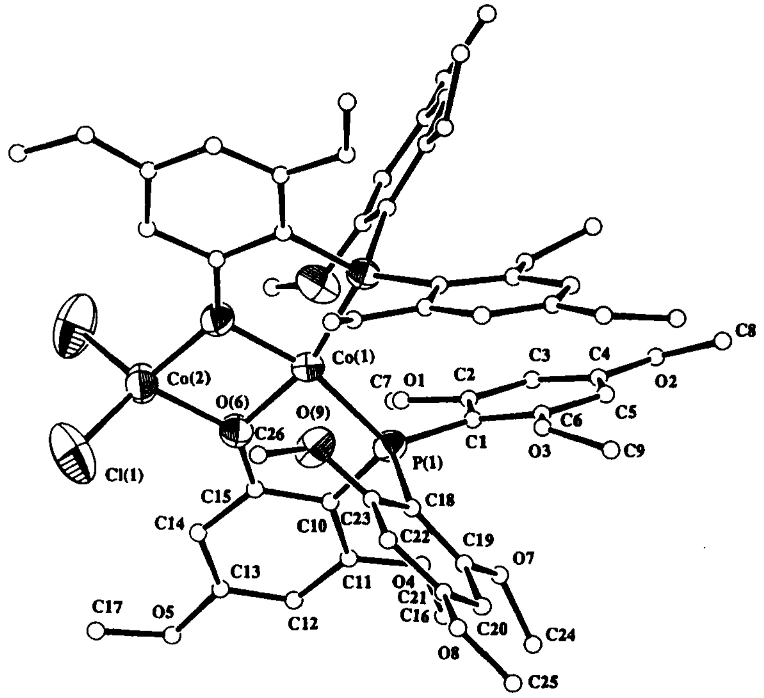


FIGURE 15 ORTEP drawing of $Cl_2Co_2\{\mu\text{-}\eta^2\text{-}(TMPP\text{-}O)_2\}$ with both tetrahedral and square planar Co(II) centers.

very reactive. Notwithstanding, we found that no reaction occurs between $Co(TMPP\text{-}O)_2$ and O_2, CO or CO_2 under ambient conditions. Evidently the metal is quite stable in the P–O ligand environment. It would appear that most reactions of this species will be ligand-based at the phenoxide oxygen as in the preparation of $Cl_2MCo\{\mu\text{-}\eta^2\text{-}(TMPP\text{-}O)_2\}$ (M = Co, Mn) from $Co(TMPP\text{-}O)_2$ and MCl_2. Further chemistry of the heterobimetallic complexes at the terminal chloride sites opens up the intriguing possibility of preparing linear heterotrimetallic complexes from the $Co(TMPP\text{-}O)_2$ "synthon"; work towards this end is currently in progress.

B. (ii) Chemistry of Ni(II)/Ni(III)

In view of the promising results with Co(II) and Rh(II), we endeavored to extend this chemistry to Ni(II), a metal that has nu-

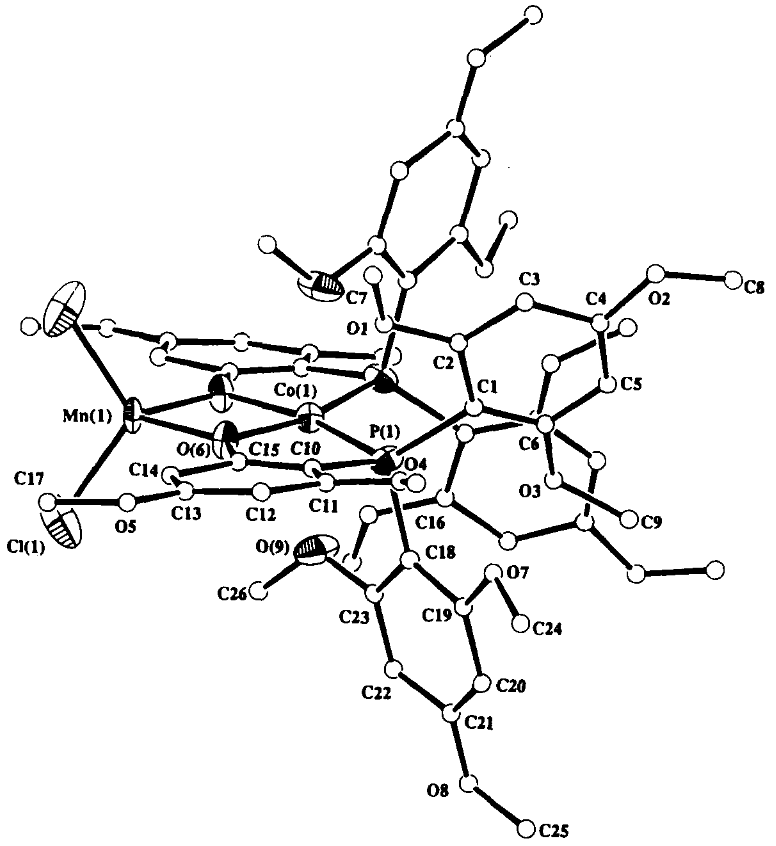


FIGURE 16 ORTEP drawing of the heterometallic dinuclear complex $Cl_2MnCo\{\mu\text{-}\eta^2\text{-}(TMPP\text{-}O)_2\}$ with a tetrahedral Mn(II) and a square planar Co(II) center.

merous catalytic and biological applications. We had already noted that (P,O) ligands were reported to have a selectivity-enhancing effect in the nickel-catalyzed oligomerization of ethene.[32] The neutral bis-phosphine compound $Ni(TMPP\text{-}O)_2$ was prepared by the reaction of the solvated salt $[Ni(MeCN)_6][BF_4]_2$ with 4 equivalents of TMPP in acetone, giving the phosphonium salt $[CH_3\text{-}TMPP][BF_4]$ as the by-product (Eq. (17)).

$$[Ni(MeCN)_6][BF_4]_2 + 4\ TMPP \xrightarrow[\text{r.t., 24 h}]{\text{Acetone}} \underset{\text{(60\% yield)}}{Ni(TMPP\text{-}O)_2} + 2\,[CH_3\text{-}TMPP][BF_4] \quad (17)$$

As Fig. 17 clearly shows, the Ni(II) complex exhibits a square-planar geometry with two trans phosphorus atoms. The Ni(II) center is further attached to oxygen atoms from two demethylated methoxy groups in the ortho position. Although numerous Ni(II)(P,O) complexes have been reported, with one exception, the only structurally characterized examples are those of general formula $NiX_2(P,O)_2$ (X = Cl, Br, I, SCN).[33-36] The use of a fluoro-alcohol diarylphosphino ligand afforded the stabilization of a homoleptic trans four-coordinate bis-(P,O) ligand Ni(II) complex which was structurally characterized.[37]

We were very interested to note that Ni(TMPP-*O*)$_2$ exhibits a very accessible, reversible oxidation at −0.07 V vs. Ag/AgCl, which allows for ease of chemical oxidation. Accordingly,

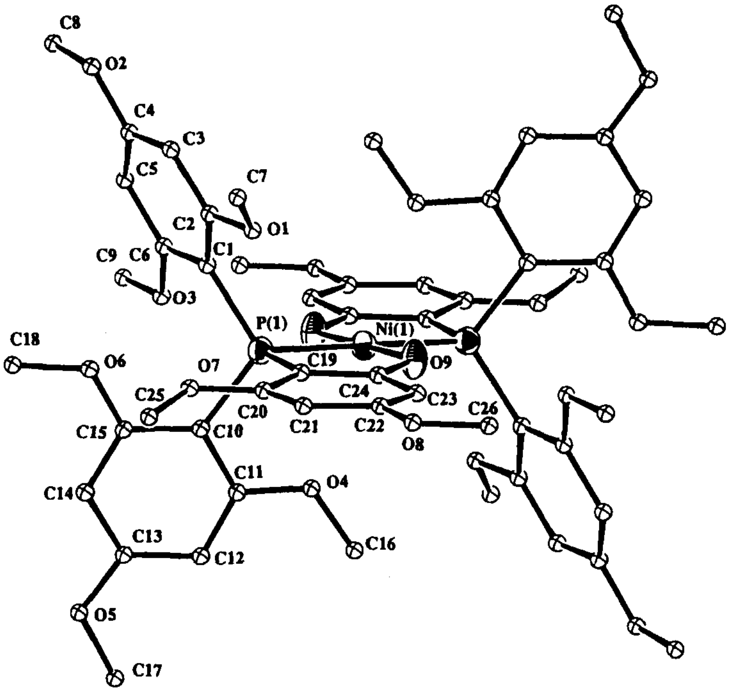


FIGURE 17 ORTEP drawing of the neutral phosphino-phenoxide complex Ni(TMPP-*O*)$_2$.

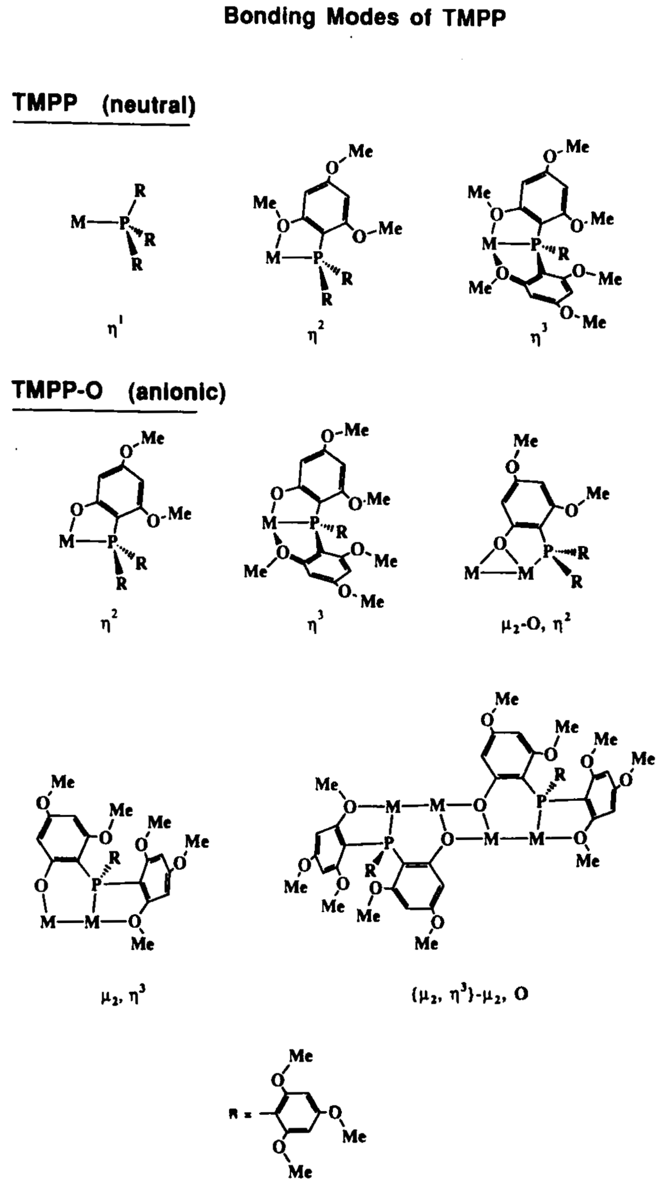


FIGURE 18 Schematic representations of the bonding modes observed in structures containing the neutral form of TMPP and the anionic phenoxide form of the ligand (TMPP-*O*).

$Ni^{II}(TMPP\text{-}O)_2$ reacts with one equivalent of the mild oxidant ferrocenium to form $[Ni^{III}(TMPP\text{-}O)_2][BF_4]$ as shown in Eq. (18) which was characterized by EPR spectroscopy and magnetic susceptibility measurements; these confirmed the $S = 1/2$ spin state and indicated a dz^2 ground state for this d^7 complex.

$$Ni^{II}(TMPP\text{-}O)_2 + [Cp_2Fe][BF_4] \xrightarrow[\text{r.t., 30 min}]{\text{Acetone}} \underset{\text{(78\% yield)}}{[Ni^{III}(TMPP\text{-}O)_2][BF_4]} \tag{18}$$

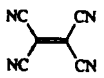
The chemistry of low-valent nickel (0 to +2) with phosphines, especially (P,O) ligands, is quite rich due to the use of nickel phosphine complexes in homogeneous catalysis,[32] but the chemistry of higher valent nickel (+3 and higher) in the presence of soft donor ligands has not been extensively developed.[38] In fact, the domain of Ni(III) chemistry has been primarily that of the bioinorganic chemists who employ biologically relevant ligands with sulfur or nitrogen donors.[39] The present work is a unique example of how the use of a bulky phosphino-phenoxide ligand can link two distinct areas of inorganic chemistry that are not ordinarily associated, thereby opening new avenues into the chemistry of Ni(III). Reactivity of the Ni(III) TMPP-*O* complex is of considerable interest and is under investigation.

The flexibility of the TMPP ligand has been well-illustrated in the examples given above. Reactions of TMPP with dinuclear compounds and with clusters have provided additional examples of bonding modes depicted schematically in Fig. 18.[14c,f,n]

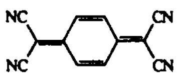
IV. APPLICATIONS

A. Polynitrile Acceptor Ligands as Linking Units in Coordination Polymers

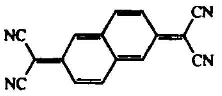
One of our present interests is the use polynitrile ligands such as those indicated schematically below as linking groups in metalloorganic polymers.



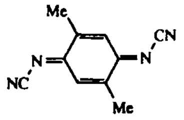
TCNE



TCNQ



TNAP



DM-DCNQI

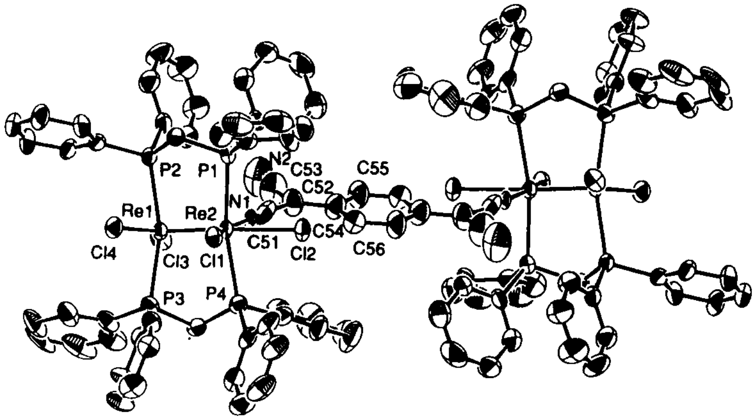


FIGURE 19 ORTEP diagram of the "dimer-of-dimers" $[Re_2Cl_4(dppm)_2]_2(\mu\text{-TCNQ})$ with a bridging TCNQ unit occupying equatorial sites of two independent Re_2 dinuclear compounds.

Using several new approaches, we are synthesizing two main types of materials; these are (1) covalently-linked and electronically coupled oligomers and polymers consisting of alternating M_2 and π-organic groups and (2) network polymers comprised of mononuclear or metal–metal bonded units cross-linked in a grid-type array with polycyano aromatic connector groups. Several exciting results have emerged from this work including the synthesis of the unprecedented TCNQ-bridged charge-transfer complex $[Re_2Cl_4(dppm)_2]_2(\mu\text{-TCNQ})$, TCNQ = (7,7′,8,8′-tetracyanoquinodimethane) (Fig. 19).[40] This chemistry takes advantage of the well-known tendency for the triply-bonded complex $Re_2Cl_4(dppm)_2$ ($E_{1/2}(ox) = +0.35$ V vs. Ag/AgCl) to form adducts with nitriles and to undergo a facile one-electron oxidation (Eq. (19)).[41]

$$Re_2Cl_4(dppm)_2 + 2TCNQ \xrightarrow{THF} \underset{\text{black crystalline solid}}{[Re_2Cl_4(dppm)_2]_2(TCNQ)} \qquad (19)$$

The magnetic, EPR, electrical and optical properties of this unusual "dimer-of-dimers" collectively point to charge delocalization. A polymeric form of the complex may be synthesized by using a 1:1 ratio of donor (Re_2) to acceptor (TCNQ) (Eq. (20)).

$$Re_2Cl_4(dppm)_2 + TCNQ \xrightarrow[\Delta,\ 1\ h]{toluene} \underset{\text{green solid}}{[Re_2Cl_4(dppm)_2](TCNQ)} \qquad (20)$$

Different phases are possible with only slight variations in the stoichiometry. Similar reactions occur with the dicyano molecule DM-DCNQI (2,5-dimethyl-N,N′-dicyanobenzoquinone diimine). The use of other metal–metal bonded precursors such as $Mo_2Cl_4(P\text{–}P)_2$ (P–P = dppm, dmpm) and the fully solvated complexes $[M_2(MeCN)_{10}]^{4+}$ (M = Mo, Rh) also leads to novel σ-coordinated forms of TCNQ, TCNE (tetracyanoethylene) and DM–DCNQI as evidenced by infrared spectroscopy in the ν(CN) region which is diagnostic for the oxidation state and bonding mode of polycyanoaromatic systems. The reactions are carried out as shown below in Eq. (21) with the non-coordinating BF_4^- anions being quantitatively exchanged for the coordinating $TCNQ^-$ groups.

$$[M_2(MeCN)_{10}][BF_4]_4 + 4(n\text{-}Bu_4N)^+(TCNQ)^- \xrightarrow{CH_3CN} M_2(TCNQ)_4 + 4(n\text{-}Bu_4N)(BF_4) \qquad (21)$$

$$(M = Mo, Rh)$$

The absence of both Bu_4N^+ and CH_3CN in the product supports a formulation of $M(TCNQ)_2$ or $M_2(TCNQ)_4$ (M = Mo, Rh). The broad and shifted $\nu(C{\equiv}N)$ indicates that the cyano groups are σ-bonded to a metal atom. Efforts to crystallize these materials by electrochemical techniques are underway.[42] The resulting structures are most likely network polymers similar to those of the type $[2,3\text{-}X,Y\text{-}DCNQI]_2M$ reported recently by Hünig and co-workers which are 1-D semiconductors for M = Li, Na, K and Ag and a 3-D metallic material for M = Cu.[43] Other recent reports of covalently bound cyano acceptor ions include the ferromagnetic material $V(TCNE)_x \cdot \gamma(CH_2Cl_2)$ ($x \sim 2$; $\gamma \sim 1/2$) thought to consist of a 3-D network of V cations bridged by σ-bonded $TCNE^{\cdot-}$ groups and the polymeric TCNE complex of Cu(II).[44,45] It appears that metal σ-bonded polycyanoacceptor polymers are a relatively undeveloped class of materials with many potentially interesting properties. Efforts on our part demonstrate that homoleptic acetonitrile cations are excellent starting materials for this chemistry. The use of $[Rh_2(MeCN)_{10}]^{4+}$ and $[Mo_2(MeCN)_{10}]^{4+}$ as building blocks for rigid porous materials[46a] and magnetic and photochemically active layered materials have been reported by two other groups.[46b,c]

B. Synthesis and Thermal Decomposition Studies of $[M_2(MeCN)_{10}][M'_6O_{19}]_2$ (M = Mo, Re, Rh; M′ = Mo, W)

We have found that dinuclear acetonitrile cations that are cocrystallized with polyoxometalate anions $[M_6O_{19}]^{2-}$ (M = Mo, W) exhibit quantitative loss of acetonitrile upon heating. For example, a TGA of $[Rh_2(MeCN)_{10}][Mo_6O_{19}]_2$ under N_2 leads to a 17.20% weight loss corresponding to loss of all nitrile groups (calculated is 17.26%) (Eq. (22)). Similar behavior was observed for the salts of $[Re_2(MeCN)_{10}]^{4+}$ and $[Mo_2(MeCN)_{10}]^{4+}$.

$$[M_2(NCCH_3)_x][Mo_6O_{19}]_2 \xrightarrow[350°C]{\text{TGA, } N_2 \atop \text{Rate} = 1°/\text{min}} \text{"}M_xMo_yO_z\text{"} \qquad (22)$$

(M = Rh, Mo, Re; x = 8, 10)

M = Rh, Re: isolated as amorphous black solids
M = Mo: crystalline blue material

As the TGA in Fig. 20 indicates, the curve shows several steps corresponding to the initial loss of four MeCN groups with subsequent loss of six, eight and finally ten ligands. X-ray powder diffraction of the desolvated material revealed amorphous behavior in the case of the Rh_2^{4+} and Re_2^{4+} salts, but in the case of $[Mo_2(MeCN)_{10}][Mo_6O_{19}]_2$, thermal treatment yields a dark blue crystalline material. The peak positions and indices constitute a unit cell of orthorhombic symmetry; work is in progress to elucidate the structure of the material.

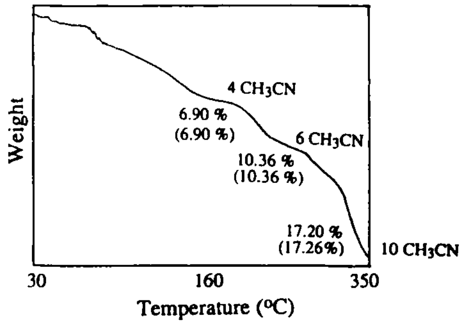
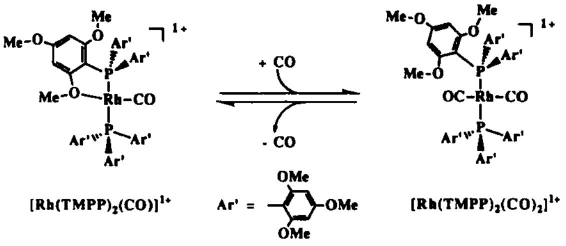


FIGURE 20 Graph of the thermogravimetric analysis curve for $[Rh_2(MeCN)_{10}]$-$[Mo_6O_{19}]_2$ emphasizing the sequential loss of all ten MeCN groups.

It appears from preliminary XPS studies that the materials obtained by mild thermal decomposition of the polyoxometallate salts are free from carbon or nitrogen containing impurities. The desolvation of the Rh and Re compounds yields materials of general formulae $Rh_xMo_yO_z$ and $Re_xMo_yO_z$, with the ratios of metals and oxygen being set by the stoichiometry of the original salt. To our knowledge, there is only one documented example of a ternary rhodium oxide, whereas instances of mixed ReMo oxides have never been reported. The advantage of the present method is that low temperature syntheses (<350°C) provide materials in which the constituent metals are mixed evenly and in exact proportions throughout the solid. Of utmost importance is the issue of purity which is being addressed by the application of TEM as well as by the use of techniques such as XPS, neutron scattering and EXAFS.

C. Development of CO Sensors Based on Ether–Phosphine Metal Complexes

In the course of investigating the chemistry of $[Rh(\eta^3\text{-TMPP})_2]^{2+}$ with CO, we noted that the Rh(I) monocarbonyl complex undergoes a reversible reaction with CO in solution (Eq. (23)).



(23)

Powder and Nujol mull samples were also seen to uptake CO reversibly at atmospheric pressure. This behavior is intriguing in the context of CO sensors, particularly if the reaction of interest exhibits the combined characteristics of (a) reversibility, (b) selectivity, (c) sensitivity and (d) ease of detection. Our initial findings prompted us to investigate the incorporation of the cation in a porous material that would trap the reactive molecular species. The use of sol-gel techniques provides for the immobilization of a sensing molecule in an environment that can be probed both by spectroscopic and electrochemical techniques, while the porous nature of the films permits facile diffusion of an exogenous substrate, such as CO, that can then bind to the sensing molecule. Previous work has demonstrated the general usefulness of sol-gel derived glasses for the encapsulation of guest molecules such as inorganic clusters, porphyrins, and lanthanide cryptate complexes.[47]

Thin film composites that are capable of reversibly sensing carbon monoxide were designed by incorporation of the Rh(I) complex into sol-gel derived titania and zirconia glass films. The considerable porosity of these films (pore sizes in the range 10–30 Å) allows for the diffusion of CO through the matrix to form the Rh(I) dicarbonyl complex $[Rh(TMPP)_2(CO)_2][BF_4]$. The binding of CO in these films results in dramatic spectroscopic and electrochemical changes that were monitored by a variety of techniques including infrared and electronic spectroscopies and cyclic voltammetry. The success of this chemistry is a direct consequence of an exceedingly labile metal–ether bond, which facilitates substitution reactions even in the solid state. The composite films are selective towards CO as they do not add O_2, CO_2, N_2 and H_2 under ordinary atmospheric conditions. On the basis of these preliminary results, the development of other small molecule sensors using molecular composites of ether–phosphine complexes appears attractive.

V. CONCLUDING REMARKS

Our investigations have unearthed a wealth of fascinating unexplored transition metal chemistry involving nitrile and ether groups. General synthetic strategies into homoleptic nitrile complexes of dinuclear cations opens up possibilities for introducing the M–M unit into new ligand environments under mild conditions, including those of interest to coordination, organometallic and materials chemists. Given the fact that Mo_2^{4+}, Re_2^{4+} and Rh_2^{4+} are stable "naked" dinuclear species, it is reasonable to expect that examples will also be found for other metals that exhibit extensive metal–metal bonding. The chemistry of the remarkable species $[Re_2(MeCN)_{10}]^{4+}$ remains to be explored, but based on the "exposed" nature of the triple bond in this molecule we expect to uncover unusual behavior not exhibited by less activated Re_2^{4+} compounds. In the realm of ether chemistry, it is clear that ether–

phosphine ligands stabilize a diverse array of coordination and electronic environments. The bulky ether–phosphine tris(2,4,6-trimethoxyphenyl)phosphine forms d^7 complexes of Rh(II) in addition to Co(II) and Ni(III). A major theme is the flexibility of the ligand, which allows access to different oxidation states while maintaining the same ligand set, a situation that facilitates reversible binding of substrates. Unlike most other sterically hindered ligands, TMPP allows the metal complex to undergo labilization of weakly held groups and isomerization to more stable geometries. The structures of the isocyanide products in the chemistry of $[Rh(\eta^3\text{-}TMPP)_2]^{2+}$ nicely illustrate this point. It is precisely the lack of structural rigidity that permits complexes of ether–phosphines such as TMPP to undergo reversible small molecule addition reactions. Extensions to other rarely encountered mononuclear d^7 metal ions such as Ru(I), Ir(II), Pd(III) and Pt(III) are in progress. Our present strategy to accessing these systems promises to allow for the development of odd electron organometallic chemistry of the heavier elements.

Acknowledgments

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