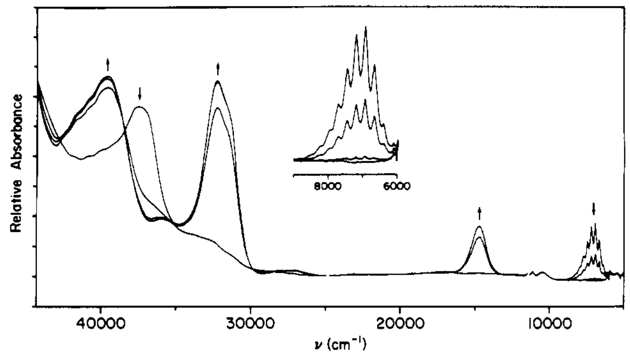

Figure 4. Spectroelectrochemical monitoring of the reversible oxidation of $Re_2Cl_8^{3-}$ to $Re_2Cl_8^{2-}$, in CH_2Cl_2/CH_3CN (1:1) and 0.5 M $[Bu_4N][BF_4]$ at 233 K. Inset: $\delta^2\delta^* \rightarrow \delta\delta^{*2}$ near-infrared band of $Re_2Cl_8^{3-}$.

Scheme I. In CH_2Cl_2 at 260 K, $Re_2Cl_8^{2-}$ exhibits a reversible reduction to $Re_2Cl_8^{3-}$ (Figure 2a) and an irreversible oxidation near 1.5 V. However, below 220 K, successive reversible oxidations to $Re_2Cl_8^{-}$ and $Re_2Cl_8^{0}$ occur in 1:1 CH_2Cl_2/CH_3CN solution, a compromise between improved solubility and elevated freezing point (Figure 2c). At 260 K, where $Re_2Cl_8^{-}$ is short-lived, $Re_2Cl_9^{-}$ forms as a daughter product ($Re_2Cl_9^{2-}$ is oxidized at the prevailing potential) and is identified by the emerging $Re_2Cl_9^{-}/Re_2Cl_9^{2-}$ couple at 0.75 V (Figure 2b).

The interconversions of $Re_2Cl_9^{z-}$ and $Re_2Cl_8^{(z-1)-}$, initially detected voltammetrically, were studied spectroelectrochemically by optically transparent thin-layer electrode (OTTLE) techniques described elsewhere.[9] Reduction of the nonahalide at −0.30 V (in CH_2Cl_2, 213 K) shows the collapse of the $Re_2Cl_9^{2-}$ spectrum and the growth of peaks at 39 900, 38 200, and 34 800 cm^{-1} attributed to $Re_2Cl_9^{3-}$. However, this spectrum rapidly gives way to the readily recognized $Re_2Cl_8^{2-}$, even though the reduction is reversible in the voltammetric time scale. Equally, in the time course of the OTTLE experiment, oxidation of $Re_2Cl_8^{2-}$ at 1.55 V at 233 K shows only the emergence of the $Re_2Cl_9^{-}$ spectrum (ece process, vide supra). In contrast, the reductions of $Re_2Cl_9^{2-}$ at 188 K and of $Re_2Cl_8^{2-}$ at 233 K show sharp isosbestic points consistent with efficient reversible generation of $Re_2Cl_9^{3-}$ and $Re_2Cl_8^{3-}$, respectively (Figures 3 and 4), according to Scheme I.

In summary, the chemical processes associated with the decomposition of electrogenerated dirhenium halide complexes are significantly retarded at low temperature, permitting recognition of four novel species in this study. There is now the prospect of rational synthetic manipulation of the dirhenium systems under suitable conditions. For example, $Re_2Cl_9^{3-}$ and $Re_2Cl_8^{3-}$ may both be accessible by chemical reduction of their corresponding dianions.

The electrochemistry of the $Re_2Cl_9^{z-}$ species parallels the recently reported[7b] behavior of the diosmium nonahalides, with the rhenium couples shifted negatively by ~0.35 V compared to the corresponding (isovalent) steps for $Os_2X_9^{z-}$. A contrary effect is seen for $Re_2X_8^{z-}$ and $Os_2X_8^{z-}$; namely, the rhenium couples are each shifted by ~+0.20 V relative to those of osmium.[10] Clearly, in the octahalides the splitting of the binuclear metal-based orbital manifold overrides the normal periodicity trends established[11] for hexahalometallates.

Upon chemical oxidation[12] with Cl_2, or one-electron electrochemical oxidation in the presence of chloride,[5] face-to-face $Re_2Cl_8^{2-}$ converts to the face-sharing bioctahedral $Re_2Cl_9^{-}$. Our results show that such a rearrangement can also be electrochemically induced with simultaneous abstraction of chloride from further $Re_2Cl_8^{2-}$. Similar behavior is observed voltammetrically in tetrahydrofuran, implying that CH_2Cl_2 is not the source of Cl^-. We do observe halide-depleted byproducts in the corresponding oxidation of $Re_2Br_8^{2-}$, and these results will be described separately. Self-abstraction of chloride ions has been reported in the electrochemical oxidation of $Re_2Cl_4L_4$ to $Re_2Cl_5L_3$ and $Re_2Cl_6L_2$ (L = PR_3).[2a]

It is remarkable that both Re_2Cl_9 and Re_2Cl_8 stoichiometries can persist over as many as four oxidation levels, Re_2^{8+} to Re_2^{5+}, even though one form is strongly preferred at each stage. The nonachloride is favored in the higher oxidation states, Re_2^{8+} and Re_2^{7+}, while the octachloride is favored for Re_2^{6+} and Re_2^{5+}. Of particular interest is the Re^{III}_2 case, where both $Re_2Cl_8^{2-}$ and $Re_2Cl_9^{3-}$ are now well characterized in solution. Electrochemically induced structural changes have been reported[7b] between the diosmium deca- and nonahalide complexes but have yet to be identified between diosmium octa- and nonahalides.

The near-infrared electronic spectrum for electrogenerated $Re_2Cl_8^{3-}$ exhibits exceptionally well-developed vibrational fine structure in solution (Figure 4). Assignment of the 6950-cm^{-1} band as a $\delta^2\delta^* \rightarrow \delta\delta^{*2}$ transition is unequivocal.[2d,3a,f] The Frank-Condon progression shows a $(Re-Re)^{5+}$ vibrational frequency of approximately 270 cm^{-1}, notably similar to the Raman absorption[13] (272–275 cm^{-1}) of $Re_2Cl_8^{2-}$. This leads to an estimated extension of ca. 0.07 Å in the Re–Re multiple bond upon electronic excitation (which involves formal reduction of the bond order by one). The δ/δ^* band of $Re_2Cl_8^{3-}$ in chloroaluminate salt solution has also been observed,[6a] although the details are not yet published. The spectrum of isoelectronic $Tc_2Cl_8^{3-}$ contains a strictly analogous band.[14] Most recently, we have characterized hitherto unknown $Re_2Br_8^{3-}$, where the corresponding band is centered at 7200 cm^{-1}.

Our data establish the stoichiometries of all species of Scheme I. Questions still remain with regard to their structures, particularly those of the $Re_2Cl_9^{0}$ to $Re_2Cl_9^{4-}$ sequence. Thus, the electrochemical reversibility of the Re_2^{8+}/Re_2^{7+} and Re_2^{7+}/Re_2^{6+} couples for the nonachloride (Figure 1a) is consistent with retention of the D_{3h} geometry[15] of $Re_2Cl_9^{-}$ but also with rapid, reversible structural rearrangements. Further studies to elucidate the electrochemically induced structural transformations of dirhenium complexes are in progress.

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Effect of Tridentate Phosphine Ligand Structure on the Basicities of Tungsten Tricarbonyl Complexes

Multidentate phosphine ligands have been used extensively[1,2] in transition-metal coordination chemistry in part because of the

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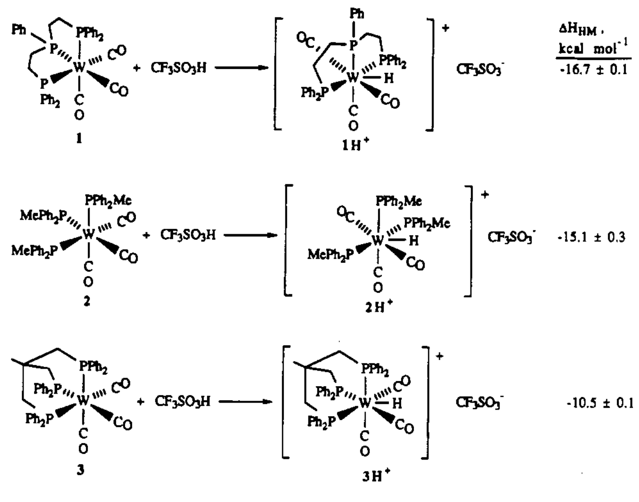
Scheme I



structural constraints that they impose on the complex. However, it is not generally known that such constraints dramatically affect the basicities of complexes toward protonation at the metal. In this communication, we report the basicities of the closely related tris(phosphine) complexes $W(CO)_3[PhP(CH_2CH_2PPh_2)_2]$ (**1**), $W(CO)_3(PPh_2Me)_3$ (**2**) and $W(CO)_3[MeC(CH_2PPh_2)_3]$ (**3**) and observe that the constraining $MeC(CH_2PPh_2)_3$ ligand decreases the basicity of the tungsten in complex **3** by 6.2 kcal mol^{-1} as compared with that in **1**, which contains the flexible tridentate $PhP(CH_2CH_2PPh_2)_2$. This remarkable decrease in basicity appears to result from a destabilization of the protonated product **3H$^+$** caused by a structural distortion forced upon the complex by the $MeC(CH_2PPh_2)_3$ ligand.

Complexes **1**,[3] **2**,[4] and **3**[5] have been prepared previously[6] and have a common *fac* structure as shown in Scheme I. Upon protonation at the tungsten with CF_3SO_3H,[6] complexes **1** and **2** form seven-coordinate products, **1H$^+$** and **2H$^+$**, in which two CO groups are proposed to be approximately trans to each other while the three phosphorus donors are approximately coplanar (Scheme I). Although the structures of **1H$^+$** and **2H$^+$** are not known in detail because they are insufficiently stable to be isolated and characterized crystallographically they do have similar structures based on similarities of their ν(CO) patterns and wavenumbers.[7] In contrast, the ν(CO) pattern of **3H$^+$** is significantly different,[7] which suggests that this complex adopts a structure different from that of **1H$^+$** and **2H$^+$** as a result of the constraint imposed by the $MeC(CH_2PPh_2)_3$ ligand which forces the phosphorus donors to remain mutually cis (Scheme I).

The basicities of **1**–**3** were determined by measuring their heats of protonation (ΔH_{HM}) by calorimetric titration with CF_3SO_3H (0.1 M)[8] in 1,2-dichloroethane (DCE) solvent at 25.0 °C under an argon atmosphere (Scheme I).[9,10] Plots of temperature vs amount of acid added were linear, indicating the complexes are protonated rapidly and quantitatively with 1 equiv of CF_3SO_3H as established previously[6] by IR and ^1H NMR spectroscopy. Furthermore, there was no decomposition of either the neutral or the protonated tungsten complexes during the titration experiment as evidenced by normal pre- and post-titration baseline slopes. The error limits (Scheme I) are average deviations from the mean ΔH_{HM} value obtained from at least four titrations. The ΔH_{HM} values, ranging from −10.5 kcal mol^{-1} for **3** to −16.7 kcal mol^{-1} for **1**, are comparable to those for the weakly basic phosphines $P(p\text{-}CF_3C_6H_4)_3$ ($\Delta H_{HM} = -13.6$ kcal mol^{-1}; $pK_a = -1.32$) and $P(p\text{-}ClC_6H_4)_3$ ($\Delta H_{HM} = -17.9$ kcal mol^{-1}; $pK_a = 1.03$).[10] Deprotonation of **1H$^+$**–**3H$^+$** with 1,3-diphenylguanidine base occurs rapidly and quantitatively permitting recovery of **1**–**3** as their *fac* isomers.

Of particular interest is the much higher basicity of **1** (−16.7 kcal mol^{-1}) with the flexible $PhP(CH_2CH_2PPh_2)_2$ tridentate ligand as compared with that for **3** (−10.5 kcal mol^{-1}) with a *fac*-coordinating ligand. The 6.2 kcal mol^{-1} higher basicity for **1** means that the equilibrium constant for the protonation of **1** is 3.5×10^4 times larger than that of **3**, assuming $\Delta S°$ values for both protonations are the same, which is nearly true for protonations of other structurally related compounds.[9] Thus, by changing the tridentate phosphine to a more flexible analogue, the basicity of the metal has been enhanced substantially.

The origin of this effect is probably not a difference in energies of the starting complexes **1** and **3** since both have *fac* geometries. It therefore seems likely that it is caused by a difference in energies between the **1H$^+$** and **3H$^+$** products, which have different structures. The most stable geometry is presumably that of **1H$^+$** since this is the one adopted by the flexible $PhP(CH_2CH_2PPh_2)_2$ ligand, as well as that assumed by complex **2** with monodentate ligands. Therefore, the most reasonable explanation for the lower basicity of **3** is that its protonated product **3H$^+$** is forced to adopt a relatively unstable structure by the restrictive $MeC(CH_2PPh_2)_3$ ligand.

Another interesting, but less dramatic, comparison is that of ΔH_{HM} values for **1** (−16.7 kcal mol^{-1}) and **2** (−15.1 kcal mol^{-1}). Complex **1** with the flexible $PhP(CH_2CH_2PPh_2)_2$ ligand is slightly more basic (1.6 kcal mol^{-1}) than **2** with monodentate phosphine ligands. The reactants and protonated products of both of these complexes have similar structures; so major structural differences do not explain the difference in ΔH_{HM} values. However, the $PhP(CH_2CH_2PPh_2)_2$ ligand is possibly a stronger donor than three PPh_2Me ligands based on the higher heat of reaction (ΔH_{rx})[11] for the displacement (eq 1) of benzene from $(C_6H_6)Mo(CO)_3$ by

$$(C_6H_6)Mo(CO)_3 + L_3 \rightarrow Mo(CO)_3(L_3) + C_6H_6;\ \Delta H_{rx} \qquad (1)$$

$$L_3 = PhP(CH_2CH_2PPh_2)_2;\ \Delta H_{rx} = -46.0 \text{ kcal mol}^{-1}$$

$$L_3 = 3\ PPh_2Me;\ \Delta H_{rx} = -42.2 \text{ kcal mol}^{-1}$$

$PhP(CH_2CH_2PPh_2)_2$ (−46.0 kcal mol^{-1}) than by three PPh_2Me ligands (−42.2 kcal mol^{-1}). Thus, the 1.6 kcal mol^{-1} greater basicity of **1** as compared to **2** may result from the greater donor ability of $PhP(CH_2CH_2PPh_2)_2$. It is also possible that small structural differences between **1** and **2** or **1H$^+$** and **2H$^+$** could account for **2** being less basic than **1** especially since **2H$^+$** is probably more sterically crowded than **1H$^+$**.

In conclusion, we observe that the basicity of the metal in $W(CO)_3$(tridentate phosphine) can be decreased by 6.2 kcal mol^{-1}

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(7) Pertinent spectroscopic data for **1**–**3**, and **1H$^+$**–**3H$^+$** are as follows. **1**: IR (CH_2Cl_2) ν(CO) 1932 (s), 1834 (s, br) cm^{-1}. **2**: IR (CH_2Cl_2) ν(CO) 1931 (s), 1832 (s, br) cm^{-1}. **3**: IR (CH_2Cl_2) ν(CO) 1930 (s), 1835 (s, br) cm^{-1}. **1H$^+$**: IR (CH_2Cl_2) ν(CO) 2038 (m), 1976 (m), 1918 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ −3.78 (m, 1 H, W–H). **2H$^+$**: IR (CH_2Cl_2) ν(CO) 2034 (m), 1958 (m), 1910 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ −1.99 (m, 1 H, W–H). **3H$^+$**: IR (CH_2Cl_2) ν(CO) 2025 (s), 1954 (s), 1941 (sh) cm^{-1}; ^1H NMR ($CDCl_3$) δ −4.62 (q, J_{PH} = 21 Hz, 1 H, W–H).

(8) The titrations were performed with use of a Tronac Model 458 adiabatic titration calorimeter as previously described.[9,10] Typically a 2.6 mM solution of the tungsten complex was titrated with 0.1 M CF_3SO_3H (standardized to a precision of ±0.0002 M) at a constant buret delivery rate (0.3962 mL min^{-1}) during 3 min. The heats of reaction were corrected for the heat of dilution of 0.1 M CF_3SO_3H ($\Delta H_{dil} = -0.2$ kcal mol^{-1}).

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or a factor of 3.5×10^4 by replacing the flexible $PhP(CH_2CH_2PPh_2)_2$ ligand by the *fac*-coordinating $MeC(CH_2PPh_2)_3$. The origin of this effect is likely the destabilization of the protonated $\mathbf{3H^+}$ product by the $MeC(CH_2PPh_2)_3$ ligand which prevents the complex from achieving the more stable geometry that is accessible with the flexible ligand in $\mathbf{1H^+}$ and with monodentate phosphine ligands in $\mathbf{2H^+}$. These results establish that it is possible to change substantially the basicities of metal centers by distorting the geometry of a product or reactant with a properly chosen chelating ligand.

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A Highly Reactive Triruthenium Cluster Complex Bearing an Alkyne Coordinated in the μ_3-η^2-Perpendicular Mode

Twenty-five years after the pioneering discovery of the first ("unsaturated" alkyne) triiron nonacarbonyl complex, $Fe_3(\mu_3\text{-}\eta^2\text{-}RCCR)(CO)_9$, by Dahl et al.,[1] we report the first ruthenium compound of a related type.

The unique 46-e iron complex was originally regarded as a curiosity, in that its alkyne moiety was found to lie perpendicular to one metal–metal bond, in sharp contrast to the majority of known ruthenium or osmium complexes that are saturated 48-e species exhibiting a parallel orientation of the alkyne with respect to a metal–metal bond.[2] The coordination modes of alkynes within trimetallic ensembles were then widely discussed in the literature.[3] The perpendicular mode was found of particular interest in account of its proposed implication in the mechanism of carbon–carbon bond cleavage.[4] Surprisingly, neither the nonacarbonyltriiron complex, nor its rare analogs bearing an alkyne in the perpendicular mode[5-7] were found to exhibit the expected behavior of unsaturated species. Furthermore, all attempts to isolate the elusive unsaturated ruthenium derivative "$Ru_3(\mu_3\text{-}\eta^2\text{-}RCCR)(CO)_9$" remained unsuccessful, thus raising questions about the existence of such a compound.[8] Besides, the structure of $Os_3(\mu_3\text{-}\eta^2\text{-}RCCR)(CO)_9$ is still unknown.[9]

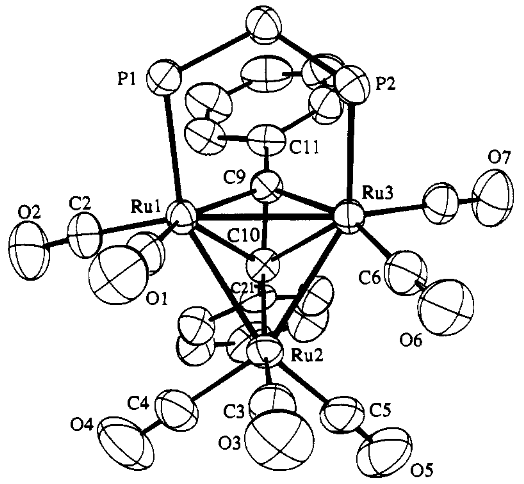
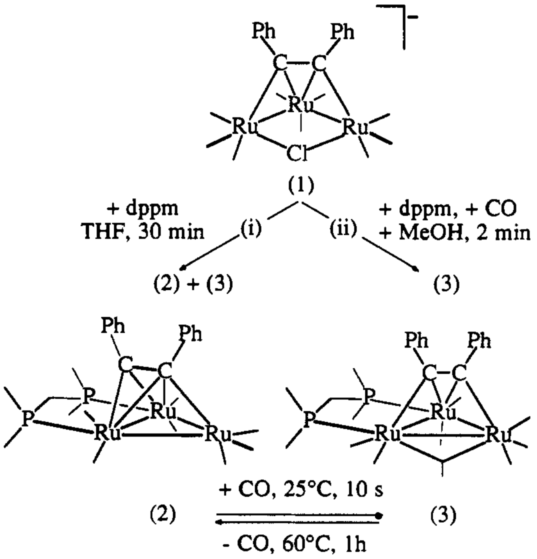


Figure 1. Perspective view of the molecular unit of the complex $Ru_3(\mu_3\text{-}\eta^2\text{-}(C_6H_5)CC(C_6H_5))(\mu\text{-}\eta^2\text{-}(C_6H_5)_2PCH_2P(C_6H_5)_2)(CO)_7$ (**2**). The four phenyl rings of the bis(diphenylphosphino)methane ligand have been omitted for clarity. Selected interatomic distances (Å) with esd's in parentheses: Ru(1)–Ru(2) = 2.6520 (6), Ru(2)–Ru(3) = 2.6683 (6), Ru(1)–Ru(3) = 2.8120 (7), Ru(1)–P(1) = 2.317 (1), Ru(3)–P(2) = 2.298 (1), Ru(1)–C(9) = 2.108 (4), Ru(3)–C(9) = 2.083 (4), Ru(1)–C(10) = 2.202 (4), Ru(3)–C(10) = 2.265 (4), Ru(2)–C(10) = 2.202 (4), C(9)–C(10) = 1.409 (6).

Scheme I



Keeping in mind the isolated observation by Smith et al.[7] that the bis(diphenylphosphino)methane- (dppm-) modified osmium derivative $Os_3(\mu_3\text{-}\eta^2\text{-}(C_6H_5)CC(C_6H_5))(\mu\text{-}\eta^2\text{-}dppm)(CO)_7$ possesses an alkyne coordinated in the perpendicular mode, we were prompted to investigate the effect of phosphine ligands on the anionic species $[Ru_3(\mu\text{-}Cl)(\mu_3\text{-}\eta^2\text{-}RCCR)(CO)_9]^-$, (**1**) which is readily available via a halide-promoted reaction of alkynes with $Ru_3(CO)_{12}$.[8]

The reaction of the PPN salt of (**1**) (PPN = bis(triphenylphosphine)nitrogen cation) with dppm was found to proceed spontaneously in THF solution at 25 °C with concomitant precipitation of (PPN)Cl. We were surprised to observe that even a 2-fold excess of dppm was rapidly consumed, leading to the

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