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Metalloradical Complexes

Access to Well-Defined Ruthenium(I) and Osmium(I) Metalloradicals**

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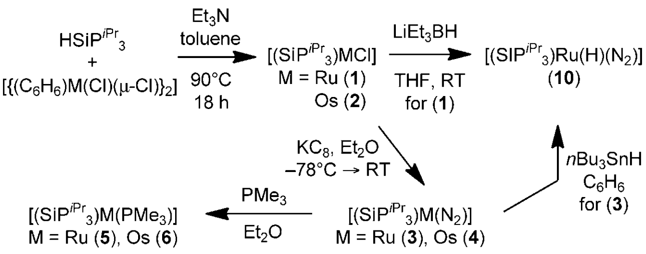
Low-valent metalloradicals of the late second- and third-row transition metals have garnered recent attention in the context of their interesting spectroscopic properties and potential applicability in catalysis.[1] Examples of mononuclear Ru^I and Os^I metalloradicals are particularly rare.[2] As these species are inherently unstable, studies that extend beyond attempts to rapidly characterize them in situ are not available. As a consequence, the chemistry of mononuclear Ru^I and Os^I complexes is essentially unexplored.[3]

Recently, we reported the first mononuclear complexes of Fe^I with terminal dinitrogen ligands.[4] The iron centers in these complexes are chelated by bulky tetradentate tris(phosphino)silyl ligands $(SiP^R_3)^-$ ($(SiP^R_3)^- = (2\text{-}R_2PC_6H_4)_3Si^-$, R = Ph, *i*Pr) that favor mono- rather than dinuclear species. The steric influence provided by this scaffold and its ability to accommodate the Fe^I oxidation state made it a plausible candidate for exploring access to the unusual oxidation states Ru^I and Os^I. Herein, we report structural, spectroscopic, and theoretical studies of well-defined and mononuclear Ru^I and Os^I complexes, $[(SiP^{iPr}_3)M(L)]$ (M = Ru, Os; L = N_2, PMe_3). To our knowledge, these complexes are the first such examples to be isolated and thoroughly characterized, including X-ray diffraction studies. Moreover, initial reactivity studies with $[(SiP^{iPr}_3)M(N_2)]$ (M = Ru, Os) complexes reveal both one- and two-electron reactivity. The latter reaction affords unusual imido complexes, $[(SiP^{iPr}_3)M(NAr)]$ (M = Ru, Os; Ar = $C_6H_4CF_3$), that display substantial "imidyl" radical character. In contrast to the highly unstable and structurally related Fe^{III} imido derivative, which can only be observed in a frozen glass,[5] these imidyl radicals are sufficiently long-lived to be isolated in pure form.

Precursors to the M^I (M = Ru, Os) complexes, $[(SiP^{iPr}_3)MCl]$ (M = Ru (**1**), Os (**2**)), were prepared by heating a mixture of $HSiP^{iPr}_3$, $[(\eta^6\text{-}C_6H_6)M(Cl)(\mu\text{-}Cl)]_2$, and Et_3N in toluene to produce red **1** and brown **2** in 94 % and 95 % yields, respectively (Scheme 1). Chemical reduction of **1** and **2** with KC_8 resulted in green $[(SiP^{iPr}_3)M(N_2)]$ (M = Ru (**3**), Os(**4**)) in 85 % and 70 % yields, respectively. The ^1H NMR spectra of **3** and **4** are similar and show broad features between $\delta = -1$–11 ppm, which is consistent with their expected paramagnetism ($S = 1/2$). The IR spectra of **3** and **4** show strong vibrations at 2088 and 2052 cm^{-1}, which correspond to the nitrogen ligands.



Scheme 1. Synthesis of mononuclear Ru^I and Os^I complexes.

Crystals suitable for X-ray diffraction were grown by slow evaporation of concentrated solutions of **3** and **4** in pentane. Unlike $[(SiP^{iPr}_3)Fe(N_2)]$, which is rigorously trigonal bipyramidal (TBP),[5] the solid-state structures of **3** (see Figure 2) and **4** (see the Supporting Information) feature substantive distortions from TBP geometries ($\tau = 0.76$ (**3**) and 0.70 (**4**))[6] with one of the P-M-P angles notably larger than the others. The N–N bond lengths are short (1.097(5) (**3**) and 1.101(6) Å (**4**)) and are consistent with the high ν_{N2} values. The N_2 ligands in **3** and **4** are labile, and addition of one equivalent of PMe_3 results in formation of the phosphine adducts, $[(SiP^{iPr}_3)M(PMe_3)]$ (M = Ru (**5**), Os(**6**)). Compound **5** has also been crystallographically characterized (see the Supporting Information) and has a geometry similar to **3** ($\tau = 0.86$).

The cyclic voltammogram of **3** shows one oxidation event at −1.24 V (vs. ferrocene/ferrocenium; Fc/Fc^+), and one reduction event at −2.14 V, which are assigned to the formal $Ru^{II/I}$ and $Ru^{I/0}$ couples, respectively. Chemical oxidation and reduction of **3** with $FcBAr^F_4$ (BAr^F_4 = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) and KC_8 leads to the corresponding Ru^{II} and Ru^0 dinitrogen complexes, $[(SiP^{iPr}_3)Ru(N_2)][BAr^F_4]$ (**7**) and $[K(THF)_x][(SiP^{iPr}_3)Ru(N_2)]$ (**8**), respectively, which have also been crystallographically characterized (see the Supporting Information). Complexes **3**, **7**, and **8** represent a rare series of mononuclear N_2 complexes that span three distinct oxidation states (Scheme 2); the related $(SiP^{iPr}_3)Fe$ system also stabilizes a corresponding N_2 series.[7] The N_2 ligand in **7** is very labile and appears to be in equilibrium with an N_2-free species,[8] as evidenced by the shift in the $Ru^{II/I}$ couple under argon and its ^{15}N NMR spectrum, which only shows resonances for the coordinated

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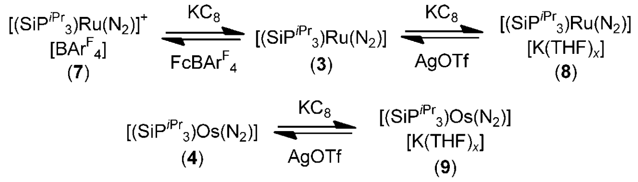


Scheme 2. Oxidation and reduction of **3** and reduction of **4**.

N_2 at low temperature.[9] While the cyclic voltammogram of **4** also displays a reduction event at −1.94 V, an irreversible oxidation event at −1.17 V is observed. The reduction product, $[K(THF)_x][(SiP^{iPr}_3)Os(N_2)]$ (**9**) was accessed in a similar procedure to that of **8** and its solid-state structure is isostructural with **8** (see the Supporting Information).

Although complexes **3**–**6** are formally Ru^I and Os^I complexes, the possibility of a ligand-centered radical cannot be excluded based on structural studies alone, especially in light of the growing recognition of redox non-innocence of many auxiliary ligands.[10] To investigate the distribution of spin density in **3**–**6**, their EPR spectra were measured at 77 K in toluene glass (Figure 1 and the Supporting Information). Each spectrum exhibits rhombic features with large hyperfine coupling to one phosphorus atom, consistent with unpaired spin density localized in an orbital of the equatorial plane of the TBP.

In assessing metal radical character, the anisotropy of the g values ($\Delta g = g_{\max} - g_{\min}$) is particularly noteworthy, since a large Δg value has been noted as a crude indication of metalloradical character for $S = 1/2$ systems.[11,12] Overall the Δg values for **3**–**6**, which are 0.135, 0.257, 0.166, and 0.318 respectively, are significantly larger than complexes that have been assigned as ligand-centered radicals.[13,14] The noticeably larger Δg values for the Os relative to the Ru complexes are likely due to a greater spin–orbit coupling constant for the heavier metal.[15] Although g values alone cannot be used as a quantitative measure of spin density, the simulated EPR parameters support our formulations of **3**–**6** as bona fide metalloradicals. As a test of our assignment, Mulliken spin densities (SD) were calculated for **3**–**6** (Figure 2 and the Supporting Information). These calculations place 76 % (**3**), 69 % (**4**), 84 % (**5**), and 79 % (**6**) of the SD at the metal center. In addition, 16 % (**3**), 15 % (**4**), 13 % (**5**), and 13 % (**6**) of the SD is located at the phosphine units.[16] In each complex, one of the P atoms possesses a greater value relative to the other two; this result is consistent with the EPR simulations that suggest an unpaired spin in the equatorial plane.

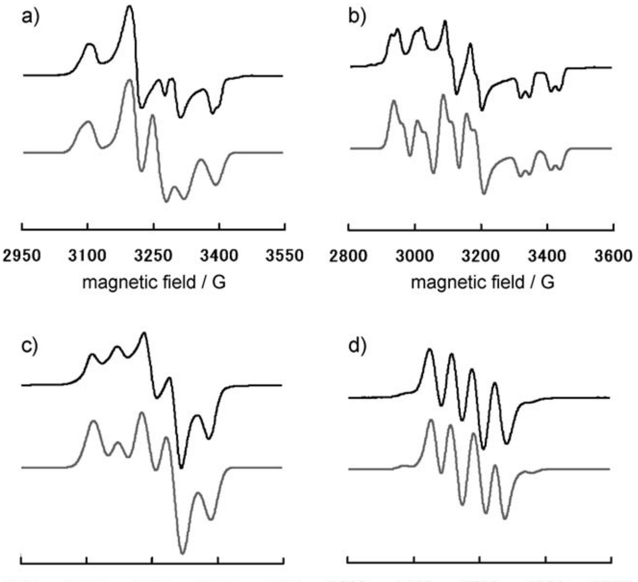


Figure 1. a) EPR spectrum of **3** (77 K). (g_x, g_y, g_z) = (2.130, 2.076, 1.995). b) EPR spectrum of **4** (77 K). (g_x, g_y, g_z) = (2.239, 2.133, 1.982) c) EPR spectrum of **5** (77 K). (g_x, g_y, g_z) = (2.175, 2.075, 2.009). d) EPR spectrum of **11** (RT). g_{iso} = 2.020. The lower curves are simulations. See the Supporting Information for other parameters.

Treatment of **3** with nBu_3SnH provided chemical evidence of its metalloradical character as the reaction cleanly afforded the hydride complex $[(SiP^{iPr}_3)Ru(H)(N_2)]$ (**10**) over 24 hours; this behavior is similar to the reactivity of other metal-centered radicals towards nBu_3SnH.[17a] In addition, **3** reacts cleanly with I_2 and PhS−SPh to afford the corresponding Ru^{II} iodide and thiolate complexes, $[(SiP^{iPr}_3)RuI]$ and $[(SiP^{iPr}_3)RuSPh]$ (see the Supporting Information).

The reactivity of late-second- and third-row metalloradicals often follows one-electron processes.[1,17] Having

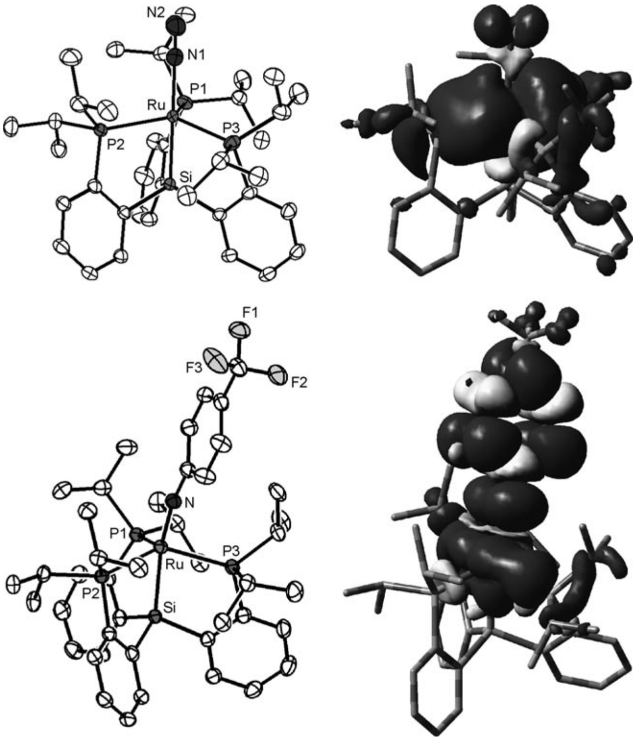
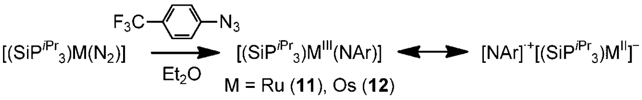


Figure 2. Solid-state structures (thermal ellipsoids set at 50 % probability) and spin density plots (0.0004 isocontours) for **3** (top) and **11** (bottom). Selected bond lengths [Å] and angles [°] for **3**: Ru–N1 2.049(3), Ru–P1 2.3221(9), Ru–P2 2.3743(9), Ru–P3 2.3253(9), Ru–Si 3.2187(9), N1–N2 1.097(5); Si-Ru-N1 177.0(1), P1-Ru-P2 109.53(3), P2-Ru-P3 131.32(3), P1-Ru-P3 111.85(3). For **11**, Ru–N 1.869(2), Ru–P1 2.2968(7), Ru–P2 2.4242(6), Ru–P3 2.3756(7), Ru–Si 2.3949(6); Si-Ru-N 162.4(1), Ru-N-C(Ar) 172.0(2), P1-Ru-P2 106.30(2), P2-Ru-P3 130.24(2), P3-Ru-P1 109.71(2).

observed one-electron reactivity in **3** we sought, in turn, to investigate whether two-electron processes might also be feasible. To this end, complex **3** was treated with organoazides to see if metal imido or nitrene species would be formed through loss of N_2, akin to the recently observed reactivity of related Fe^I complexes.[18] Treatment of **3** with *para*-CF_3-substituted phenylazide led to formation of the formally Ru^{III} imido species, $[(SiP^{iPr}_3)Ru(NAr)]$ ($Ar = C_6H_4CF_3$; **11**; Scheme 3). The solid-state structure of **11** (Figure 2) reveals a geometry midway between TBP ($\tau = 0.54$) and square pyramidal with a Ru–N bond length of 1.869(2) Å. Whilst this bond length is significantly shorter than Ru–N bonds between typical ruthenium anilides (Ru–N > 1.95 Å),[19] it is appreciably longer than prototypical ruthenium imido complexes (Ru–N < 1.80 Å).[20] Treatment of **4** with *para*-CF_3 substituted phenylazide also leads to the corresponding Os^{III} imido species $[(SiP^{iPr}_3)Os(NAr)]$ ($Ar = C_6H_4CF_3$; **12**). Crystallographic characterization established that **12** is isostructural to its ruthenium analogue **11** (see the Supporting Information).

Complexes **11** and **12** represent interesting examples of five-coordinate, formally d^5 imido complexes. Qualitative molecular orbital diagrams predict low bond orders (less than or equal to 1.5) because of the occupation of π^* orbitals.[21] It is emphasized that TBP complexes with metal–ligand multiple bonds and d-electron configurations greater than 1 are virtually unknown. Que and co-workers have reported a noteworthy recent exception.[22] The stability of **11** and **12** is, therefore, surprising and distinct from its chemically related and highly unstable iron derivative $[(SiP^{iPr}_3)Fe(N\text{-}p\text{-tolyl})]$, which has a calculated geometry[23] close to **11** and **12**. $[(SiP^{iPr}_3)Fe(N\text{-}p\text{-tolyl})]$ is only observable by EPR when generated photolytically in a frozen glass, and decomposes rapidly by presumed bimolecular nitrene coupling to yield azobenzenes.[5] While complexes **11** and **12** decompose in solution at room temperature over several days, they are stable at −35 °C as solids for extended periods.

The difference in stability/reactivity between $[(SiP^{iPr}_3)Fe(N\text{-}p\text{-tolyl})]$ and complexes **11** and **12** could potentially be attributed to differences in electronic configuration. Though they are formally M^{III} imido complexes, close examination of their EPR spectra indicate that they possess significant nitrogen-centered radical character. Unlike the spectra of **3**–**6**, which show broad features at room temperature, the spectra of **11** and **12** (Figure 1 and the Supporting Information) show relatively sharp four-line patterns with isotropic *g* values of 2.02 and 2.01, respectively, which are much closer in value to that of a free electron ($g_e = 2.0023$) compared to the corresponding metalloradicals **3**–**6**. Ruthenium and osmium hyperfine coupling are also observed ($A^{Ru} = 48$ MHz (**11**), $A^{Os} = 150$ MHz (**12**)) and the spectra are best simulated by assigning hyperfine coupling to one nitrogen atom ($A^N = 98$ MHz (**11**), $A^N = 93$ MHz (**12**)) and smaller coupling to one phosphorus atom ($A^P = 64$ MHz (**11**), $A^P = 58$ MHz (**12**)). These isotropic A^N values are surprisingly large. For comparison, the similarly sp-hybridized NO radical has a nitrogen hyperfine coupling constant of $A^N = 77$ MHz.[24] In addition, the Ru hyperfine coupling constant A^{Ru} in **11** is smaller than a spectroscopically detected Ru^{III} imido complex that was suggested to possess considerable ligand radical character.[25] Further supporting the largely ligand-centered radical character of **11** and **12**, the EPR spectra at 77 K reveal much smaller *g* anisotropies ($\Delta g = 0.072$ (**11**) and 0.128 (**12**)) relative to their corresponding Ru(I) and Os(I) metalloradicals **3**–**6**. DFT calculations are consistent with the EPR parameters and show that 54 % (**11**) and 54 % (**12**) of the SD is distributed throughout the NAr moiety, of which 27 % (**11**) and 24 % (**12**) is on the nitrogen atom and 40 % (**11**) and 39 % (**12**) is located at the metal center (see the Supporting Information). While delocalization of the spin density along the M–NAr moiety is evident, both EPR and DFT data suggest that perhaps **11** and **12** are best considered M^{II} complexes with a ligand-localized radical (Scheme 3). This ligand radical is a one-electron oxidized imido ligand $({}^{\cdot}NAr)^-$ and exhibits properties of a rare imidyl radical that has only very recently been described in coordination chemistry.[25,26] The electronic configurations of **11** and **12** distinguish themselves from $[(SiP^{iPr}_3)Fe(N\text{-}p\text{-tolyl})]$,[5] whose DFT-predicted ground state ($S = \tfrac{1}{2}$) is calculated to consist of a largely metal-centered radical.



Scheme 3. Synthesis of formal M^{III} imido complexes with significant radical character on the NAr unit.

In conclusion, we have introduced several well-defined examples of mononuclear Ru^I and Os^I complexes. These unusual complexes have been shown, through EPR measurements and DFT calculations, to consist of predominantly metal-centered radical character with a minority of the spin density delocalized onto the chelated phosphines. The reactivity of the dinitrogen adduct derivatives **3** and **4** were shown to exhibit formal $M^{I/III}$ group-transfer reactivity. Detailed analysis of the imido and nitrene products suggests that they possess substantial imidyl radical character.

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