Angewandte Chemie International Edition

DOI: 10.1002/anie.201002715

Ruthenium and Osmium Metalloradicals

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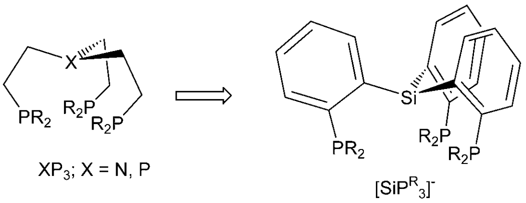
dinitrogen · non-innocent ligands · osmium · radicals · ruthenium

With a limited number of well-understood exceptions (such as the square-planar d^8 configuration and complexes with strongly π-donating ligands), complexes of transition metals that belong to the 4d and 5d series most typically follow the so-called EAN (effective atomic number) rule by adopting a closed-shell 18-electron configuration. Relative to the 3d metals, the metals of the 4d and 5d series have more diffuse and more polarizable d orbitals, leading to greater bond covalence and to lower pairing energies and consequently to lower stability for open-shell configurations, especially in the lower oxidation states and especially for the late transition metals.[1] Coordinative saturation of the metal center is achieved by coordination of a suitable number of one- and two-electron ligands and/or by forming metal–metal bonds in oligonuclear clusters. Nevertheless, enforcing mononuclear metalloradical configurations through the use of specially designed ligands can lead to peculiar properties and reactivity. A good example is the use of bulky porphyrins or geometrically constrained alkene-containing ligands to give stable porphyrin rhodium(II) complexes or alkene rhodium(II) and alkene iridium(II) complexes that have shown interesting applications in C–H activation and in catalysis.[2,3]

For the heavier Group 8 elements ruthenium and osmium, complexes with the formal oxidation state I and a metalloradical character were previously produced, generally by electrochemical methods, only as unstable species or could not be isolated. Pilloni et al. pointed out as early as 1977 that the coordination geometry could be an important factor allowing the generation of stable d^7 mononuclear complexes and that the presumed lability of the chloride ligand in complex $[Ru(dppp)_2Cl]$ (dppp = 1,3-bisdiphenylphosphinopropane) opens decomposition pathways through disproportionation.[4] A longer-living but still not isolable ruthenium(I) complex, $[Ru(PP_3)Cl]$,[5] was obtained by using the "Sacconi-type" tetradentate phosphine ligand $PP_3 = P(CH_2CH_2PPh_2)_3$, which is known to stabilize $M(L_4)$ moieties either in an octahedral (with two additional *cis* ligands) or in a trigonal-bipyramidal (with one additional axial ligand) coordination geometry. A key to further stabilize the construct could be the incorporation of the anionic function into the tetradentate ligand to yield a $M(XL_3)$ moiety. On the basis of this idea, Peters has recently developed tris(*o*-phosphinophenyl)silyl ligands (their relationship to the Sacconi system is illustrated in Scheme 1), and shown that they are capable of stabilizing dinitrogen complexes of Fe^I, $[(SiP^R_3)Fe(N_2)]$, with R = Ph or *i*Pr.[6–8]



Scheme 1. Relationship between Sacconi-type XP_3 and Peters' $[SiP^R_3]^-$ ligands.

More recently, the same ligand (with R = *i*Pr) has successfully been used to generate the first stable mononuclear ruthenium(I) and osmium(I) metalloradicals (see Scheme 2).[9] The precursor complexes $[(SiP^{iPr}_3)MCl]$ were prepared from $[\{(\eta^6\text{-}C_6H_6)MCl_2\}_2]$ and $HSiP^{iPr}_3$ in the presence of Et_3N and then converted into $[(SiP^{iPr}_3)M(N_2)]$ (M = Ru, **1**; Os, **2**) by reduction with KC_8 under dinitrogen.

The spectroscopic (IR, NMR, EPR) and structural (single crystal X-ray diffraction, see Figure 1 for **1**) characterization leaves no doubt about the formulation as mononuclear M^I species. The N_2 ligand is labile and could be substituted by PMe_3 yielding the corresponding $[(SiP^{iPr}_3)M(PMe_3)]$ complexes (M = Ru, **3**; Os, **4**), which have also been fully characterized.

The two dinitrogen complexes (**1** and **2**) were also investigated electrochemically, revealing a reduction and an oxidation. The reduction process is reversible for both compounds and the stable M^0 products could be generated by stoichiometric reductions with KC_8, isolated, and crystallographically characterized. The oxidation process is reversible only for the ruthenium species and the stable product, which contains a very labile N_2 ligand, could be obtained by stoichiometric oxidation with $[Cp_2Fe][B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]$ ($Cp = C_5H_5$).

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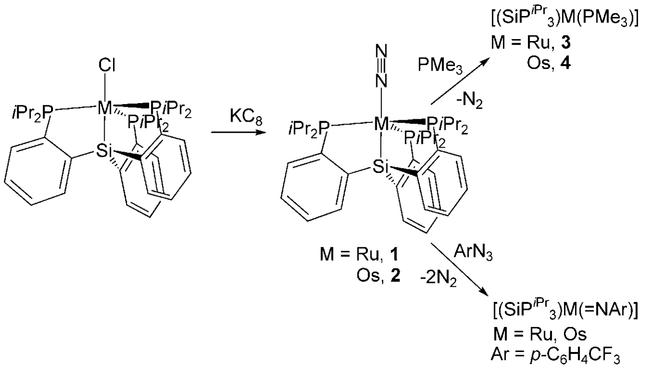


Scheme 2. Generation and reactivity of [(SiP$^{iPr}{}_3$)M(N$_2$)] complexes of ruthenium and osmium.

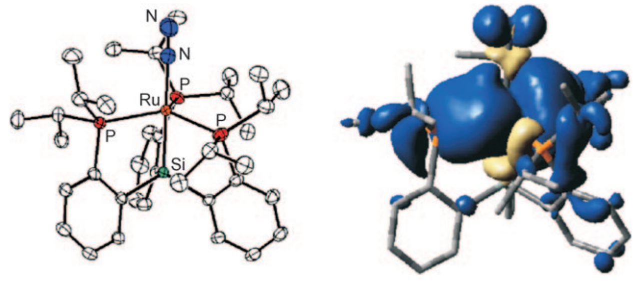
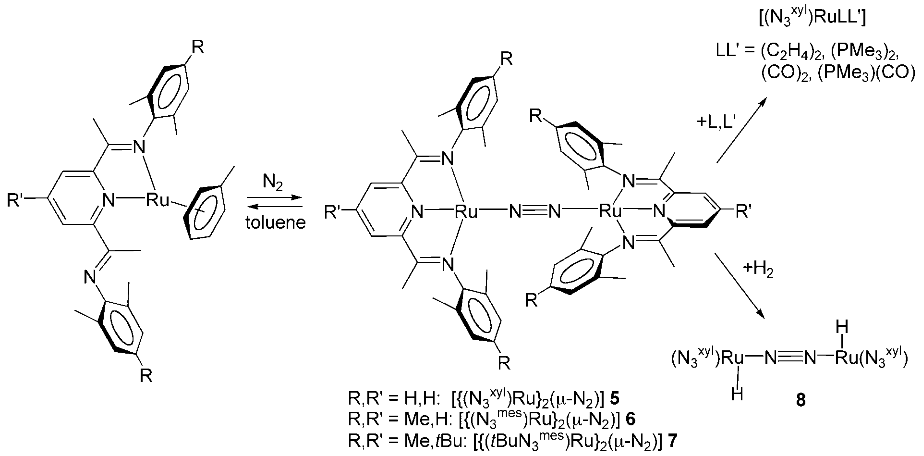


Figure 1. X-ray structure and spin-density plot for compound **1**.

The radical character at the metal is indicated by the chemical reactivity for compound **1**, that is, by the generation of the Ru^{II} complexes [(SiP$^{iPr}{}_3$)RuH(N$_2$)], [(SiP$^{iPr}{}_3$)RuI], and [(SiP$^{iPr}{}_3$)Ru(SPh)] upon treatment with Bu$_3$SnH, I$_2$, and PhSSPh, respectively. However, two-electron reactivity is also shown (in addition to the above described transformation to **3** and **4**) by the reactions of **1** and **2** with organoazides, leading to imido/nitrene products by elimination of N$_2$ (Scheme 2).

The EPR investigation and DFT calculations for compounds **1–4** give strong support to the description of the complexes as genuine metalloradicals. The EPR spectra show significantly anisotropic rhombic tensors with larger ($g_{max}-g_{min}$) values than typically observed for ligand-centered radicals, while the calculations place the majority of the spin density (76 % for **1**, 69 % for **2**, 84 % for **3**, and 79 % for **4**) on the metal and also a non-negligible fraction at the P nuclei (Figure 1). The observed P hyperfine splitting is consistent with the unpaired electron being located in the equatorial plane.

Another recent study by Berry[10] has shown that the Ru^0 complexes [(η^6-toluene)Ru(N$_3{}^{Ar}$)], where the 2,6-diiminopyridine ligand (N$_3{}^{Ar}$) is only coordinated in a bidentate fashion, are converted under dinitrogen into the diamagnetic dinuclear [{(N$_3{}^{Ar}$)Ru}$_2$(μ-N$_2$)] complexes **5–7** (Scheme 3), where the coordination geometry of the ruthenium center is strictly square planar, an unusual observation for a formally Ru^0 center. In light of the known non-innocent character of 2,6-diiminopyridine ligands and on the previous recognition that related [(N$_3{}^{Ar}$)FeCl] and [(N$_3{}^{Ar}$)Fe(N$_2$)$_2$] complexes are best described as Fe^{II} complexes with transfer of one or two electrons to the ligand,[11,12] the electronic structure of compounds **5–7** has been carefully analyzed. Structural evidence (ligand imino C=N distances) and an unusual temperature independent shift of the imine methyl proton resonance in the ^{1}H NMR spectrum suggest a certain degree of ligand non-innocence. Replacement of the N$_2$ ligand in compound **5** by other neutral donors (C$_2$H$_4$, PMe$_3$, CO) yields five-coordinate complexes [(N$_3{}^{xyl}$)RuLL′] (Scheme 3) that seem adequately described as Ru^0 derivatives. On the other hand, the addition of H$_2$ affords an unusual dinuclear ruthenium hydride complex [{(N$_3{}^{xyl}$)RuH}$_2$(μ-N$_2$)] (**8**; Scheme 3), the structure of which shows two square-pyramidal ruthenium centers, each with an axial hydrido ligand; the metal centers are linked by a linear N$_2$ bridge.[13] This complex is formally a Ru^I species and is indeed paramagnetic as expected for one unpaired electron per {(N$_3{}^{xyl}$)Ru(H)} unit, but it displays no tendency to further add H$_2$ to yield a dihydrido Ru^{II} product. Broken-symmetry DFT calculations on a mononuclear [(N$_3{}^{xyl}$)Ru(H)(N$_2$)] model complex reveal a large contribution of the Ru^{II}/(N$_3{}^{Ar}$)$^-$ formalism, with 73 %



Scheme 3. Generation and reactivity of [(SiP$^{iPr}{}_3$)M(N$_2$)] complexes.

singly occupied molecular orbital (SOMO) localization on the (N_3^{Ar}) ligands and only 19% on the metal centers. In conclusion, the one-electron reactivity of **5** with H_2 appears more consistent with a formal transformation of **5** from a Ru^I to Ru^{II} species rather than from Ru^0 to Ru^I.

In conclusion, the two above-highlighted elegant studies by Peters and Berry have underlined for the first time that relatively stable complexes of ruthenium and osmium in the oxidation state I may be obtained by judicious choice of the supporting ligand system, but also that internal electronic rearrangements are possible when the ligand has the ability to play a non-innocent role. They have clearly shown the need to carefully apply a vast array of experimental and theoretical characterization methods to gain an appropriate description of the electronic structure for these interesting new systems.[9,10,13] The preliminary reactivity studies already announce that these species are amenable to the development of interesting new chemistry. Note that a recent Review on ruthenium complexes with non-innocent ligands has appeared,[14] although it makes no mention of systems best described as having a ruthenium center with a formal oxidation state of I.

Received: May 5, 2010

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