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Synthesis of the Ru^{IV} amido complex $[TpRu(CO)(PPh_3)(NHPh)][OTf]_2$ (Tp = hydridotris(pyrazolyl)borate; OTf = trifluoromethanesulfonate) and deprotonation to form an octahedral and d^4 imido complex: computational study of Ru^{IV}–imido bonding†

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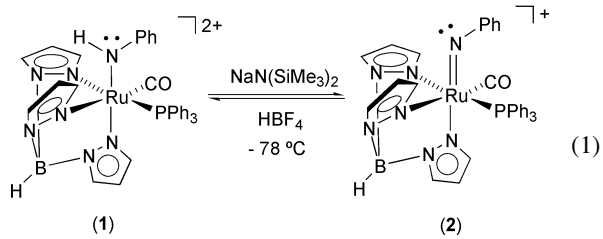
Deprotonation of $[TpRu(CO)(PPh_3)(NHPh)][OTf]_2$ yields the thermally unstable d^4 imido complex $[TpRu(CO)(PPh_3)(NPh)][OTf]$; a computational study of the bonding of the imido complex provides a foundation for discussion of its instability in terms of π-conflict.

Complexes possessing imido ligands are known for most of the transition series, and imido moieties are of interest as both inert ancillary ligands as well as for their potential synthetic value in nitrene transfer, imine metathesis, and C–H activation reactions.[1–6] Monomeric imido complexes of late transition metals are relatively rare, and it has been suggested that the paucity of late metal imido complexes (and other π-donating ligands) could be due, at least in part, to the presence of π-conflict between filled dπ orbitals and the π-donating ligands.[7,8] However, questions remain concerning the role of π-conflict in the bonding and reactivity of such systems. To our knowledge, only a few octahedral and d^4 imido complexes have been implicated as intermediates in reactions, and an isolable complex has never been described.[9–13]

Reaction of the amido complex $[TpRu^{II}(CO)(PPh_3)(NHPh)]$ with two equivalents of AgOTf in the presence of excess base (Et_3N or 2,6-lutidine) in CH_2Cl_2 yields $[TpRu^{IV}(CO)(PPh_3)(NHPh)][OTf]_2$ (**1**), and counter ion metathesis with $NaBAr'_4$ (Ar′ = 3,5-$(CF_3)_2C_6H_3$) produces $[TpRu^{IV}(CO)(PPh_3)(NHPh)][BAr'_4]_2$ (**1-BAr′$_4$**).[14] The ^1H NMR spectrum of **1** exhibits two broad resonances at approximately 10.15 ppm that integrate for a combined total of one proton. The Tp and PPh_3 resonances are broad at room temperature, and lowering the temperature of the NMR solution results in further line broadening of these resonances. Heating the solution results in coalescence of the downfield amido NH resonances into a single resonance and sharpening of the Tp and PPh_3 resonances. These results are consistent with two isomers due to restricted rotation around the Ru–N_{amido} bond, and the rotational barrier can be approximated to be 74 kJ mol^{-1} from the coalescence temperature of the resonances due to the amido proton (K_{eq} = 1 at room temperature). Amido to metal π-donation likely contributes to the rotational barrier since the corresponding Ru(II) amido complex has a smaller barrier to rotation.[14] Addition of $[D_4]$-methanol to a CD_2Cl_2 solution of **1** results in the disappearance of the downfield amido resonances in the ^1H NMR spectrum within 12 hours at room temperature (no other changes are noted). The two amido proton resonances of the ^{15}N labeled complex $[TpRu^{IV}(CO)(PPh_3)(^{15}NHPh)][OTf]_2$ are doublets at room temperature ($^1J_{NH}$ 71 Hz) while the ^{13}C NMR spectrum reveals that the resonance assigned as the *ipso* carbon of the amido phenyl (171.6 ppm) is split into a doublet with $^1J_{NC}$ 12 Hz (consistent with other $^1J_{NC}$ values).[15–17]

† Electronic supplementary information (ESI) available: experimental procedures; Table 1 comparing calculated structural parameters for complex **2** *versus* data from the CSD; references. See http://www.rsc.org/suppdata/cc/b1/b110999e/

Reaction of $[TpRu^{IV}(CO)(PPh_3)(NHPh)][OTf]_2$ with $Na\{N(SiMe_3)_2\}$ in THF at −78 °C results in a color change from blue to purple and the production of $HN(SiMe_3)_2$ as well as a new Ru complex that is ^1H NMR silent. At −70 °C the new Ru complex exhibits ν_{CO} 1930 cm^{-1} in the IR spectrum (*cf.* 1996 cm^{-1} for **1**). The 66 cm^{-1} change in CO stretching frequency is likely due to the transformation from a dicationic to a monocationic complex. Treatment of a $[D_8]$-THF solution of deprotonated **1** at −78 °C with HBF_4 *cleanly and quantitatively* yields the Ru^{IV} amido complex $[TpRu^{IV}(CO)(PPh_3)(NHPh)][OTf][BF_4]$ as determined by ^1H NMR spectroscopy. These observations are consistent with the reversible (at low temperature) deprotonation of complex **1** to form the imido complex $[TpRu^{IV}(CO)(PPh_3)(NPh)][OTf]$ (**2**) (eqn (1)). The lack of resonances



(1)

in the ^1H NMR of complex **2** at low temperature suggests that this complex is paramagnetic. At temperatures above −50 °C, complex **2** decomposes to form multiple intractable products. The IR spectrum of the decomposed mixture reveals a very broad ν_{CO} 1972 cm^{-1}. The addition of HBF_4 to the reaction mixture containing complex **2** at temperatures > −50 °C results in the appearance of *multiple* intractable and uncharacterized diamagnetic complexes. All attempts to isolate complex **2** in the solid-state have failed.

A qualitative molecular orbital diagram for $[TpRu^{IV}(CO)(PPh_3)(NPh)][OTf]$ is shown in Scheme 1. The degeneracy of the octahedral dπ manifold is split by the asymmetric $\{TpRu(CO)(PPh_3)\}$ fragment, and the imido ligand then interacts with d_{xz} and d_{yz} to form two bonding and two anti-bonding combinations with a total of six electrons available to occupy these four orbitals. An important question regarding the influence of π-conflict is the extent to which the filled anti-bonding orbital is 'anti-bonding.' That is, are the electrons in MO1 (Scheme 1) better considered as a lone pair or as electrons occupying a high-energy anti-bonding orbital? If the former assertion is correct, it might be assumed that **2** would be a diamagnetic system since the ΔE between MO1 and MO2 would be large due to the discrepancy in π-acidity between CO and PPh_3. However, the apparent paramagnetic nature of **2** indicates that MO1 possesses significant anti-bonding character and a triplet ground state results. In accord with this description is the diamagnetic character of **1**. The protonation of **2** formally removes the two dπ electrons that occupy MO1 and MO2 in Scheme 1 as they are used to form the N–H σ bond.

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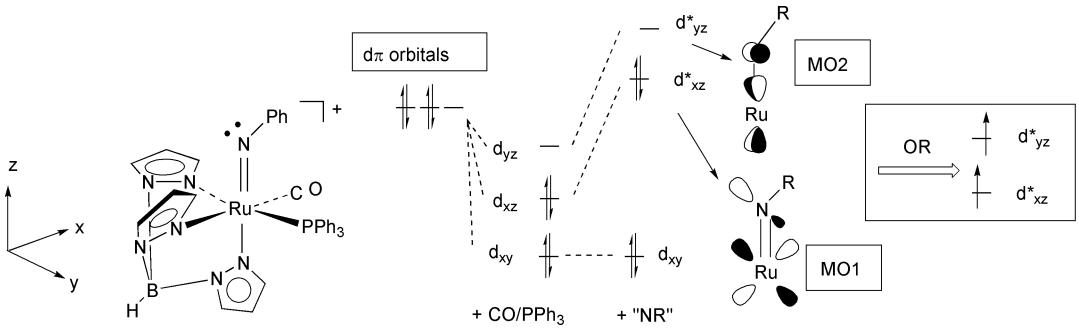

Scheme 1 Qualitative MO diagram for $[TpRu(CO)(PPh_3)(NPh)]^+$. The orbitals d^*_{yz} and d^*_{xz} are π-anti-bonding combinations.

Since there is no crystal structure of **2**, Cundari's *de novo* structural prediction methodology was used to obtain a computational model of the system.[18,19] Molecular mechanics (MM) was used to search the conformational space of **2**. Then semiempirical quantum mechanics (SEQM) was used to optimize the structure in both the singlet and triplet states. The SEQM-optimized structures were submitted to Dmol[3] for density functional theory (DFT) geometry optimization.‡ The purpose of the molecular mechanics and SEQM computations prior to DFT computations is to speed up the DFT optimization.[20]

The DFT structures‡ compare well with bond lengths and angles for related structures obtained from the Cambridge Structural Database (see ESI†).[21] The DFT calculations with the BOP functional show that the triplet state of **2** is more stable than the singlet by 0.452 eV. Since this energy difference is relatively small, single energy calculations were performed with the BLYP, GGA, and JMW functionals.§ In all cases, the triplet state was more stable than the singlet (0.514 eV for BLYP, 0.266 eV for GGA, and 1.40 eV for JMW). Finally, ONIOM calculations were performed on **2** using Gaussian 98,[22] which showed the triplet state more stable than the singlet by 0.642 eV with the B3LYP functional.¶

For the triplet state, the two singly occupied molecular orbitals (SOMOs) of **2** have energies of −7.14 and −7.75 eV whereas the two lowest energy unoccupied molecular orbitals (SUMOs) have energies at −6.36 and –6.28 eV. In the singlet state, the HOMO has an energy of −7.25 eV and the LUMO of −6.68 eV. The single electron in the d_{xz} (Scheme 1) in the triplet state is stabilized by 0.504 eV relative to the singlet state, and the electron in the d_{yz} orbital is stabilized by 0.456 eV relative to the same orbital in the singlet state. In the triplet state, the SUMO lies 0.771 eV above the SOMO whereas in the singlet state the LUMO lies 0.567 eV above the HOMO.

These results have led us to conclude that the HOMO (SOMOs for the triplet state) for **2** possesses significant anti-bonding character and that π-conflict contributes to the low thermal stability. The π-conflict between the electron density on nitrogen and the electrons in the metal-based d-orbitals destabilizes the singlet spin state (MO1 in Scheme 1). However, in the triplet state the electron density is spread between MO1 and MO2 (Scheme 1), which results in a less destabilizing interaction than in the singlet state due to the exchange integral. In contrast to imido ligands, examples of *isolable* octahedral and d^4 oxo complexes are known.[23] Perhaps the more electronegative oxygen-based ligands mitigate the interaction of ligand-based π-electrons with metal dπ-electrons and result in more stable and isolable complexes (*i.e.*, effects due to π-conflict are lessened).

In summary, generation of the octahedral and d^4 imido complex $[TpRu^{IV}(CO)(PPh_3)(NPh)]^+$ has been accomplished at low temperatures. This complex is only stable below −50 °C, and its instability is attributed to the π-conflict between a filled dπ orbital and electrons on the imido ligand. The Ru(IV) imido complex′s paramagnetic nature has been attributed to π-conflict.

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Notes and references

‡ Optimization was performed in Dmol[3] using the BOP functional, double numeric basis set with polarization functions (DNP) and VPSR relativistic pseudopotential.[24]

§ Single point energy calculations using the BLYP, GGA, and VWN functionals used a double numer basis set with double polairzation functions and the VPSR relativistic pseudopotential.[24]

¶ In the ONIOM calculations, the phenyl rings of PPh_3 ligand were treated with MM and the rest of the complex with QM.

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