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Photochemistry of a Structurally Uncomplicated Phenylcarbyne Complex

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Although synthesis and reactivity studies of transition metal−main group element multiple bonds are numerous,[1] corresponding studies of their photophysics and photochemistry are not. Of particular interest to us is the systematic comparison of both ground state and excited state chemistry of the metal−element multiple bond in similar coordination environments.[2]

We find that the recently prepared complex[3] $[PhCOs(NH_3)_5](O_3SCF_3)_3$ is luminescent in fluid solution and, as such, represents a new class of a luminescent carbyne complex. We note that there are several other examples of emissive d^2 arylcarbynes of Mo and W.[4] In addition, a number of carbyne-based photochemical reactions have been shown to occur with carbyne derivatives of Mo and W.[5] The uniqueness of the luminescent organometallic complex, $[PhCOs(NH_3)_5]^{3+}$ is in its simplicity, since the metal carbyne chromophore can be studied without spectroscopic interference of the ammines which complete the coordination sphere. Here we present the photochemistry and photophysics of the carbyne-localized excited state of $[PhCOs(NH_3)_5]^{3+}$ in CH_3CN and furthermore report a base-induced quenching process associated with the lowest excited state.

The electronic spectrum of $[PhCOs(NH_3)_5]^{3+}$ in CH_3CN exhibits a weak absorption band system at 462 nm (ϵ = 200 M^{-1} cm^{-1}) and a more intense absorption at 292 nm (ϵ = 14 300 M^{-1} cm^{-1}). The low-energy region can be assigned by comparison with the d^2 species $[NOsCl_4(H_2O)]^-$, $[NOsCl_4]^-$, and $[NOs(NH_3)_4]^{3+}$, where the lowest absorbing and emitting excited state is based on a transition that is $b_2(d_{xy}) \rightarrow e(d_{xz}, d_{yz})$ in nature.[6] For these complexes, in C_{4v} symmetry, the ordering of the orbitals is $b_2(d_{xy}) < e(d_{xz}, d_{yz}) < b_1(d_{x^2-y^2}) \leq a_1(d_{z^2})$. The d_{xy} metal orbital is nonbonding, and the d_{xz} and d_{yz} metal orbitals mix with the p_x and p_y orbitals on the N to give π and π^* orbitals of the triple bond. For the C_{2v} symmetry of the $[PhCOs(NH_3)_5]^{3+}$ complex, the e set is split into orbitals of different energies, principally by interaction with the phenyl π system. This has been demonstrated from molecular orbital calculations on a similar metal carbyne, *trans*-$PhCCr(CO)_4Cl$, by Fenski and

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Kostic, where the LUMO was shown to have significant conjugation with the π orbitals on the phenyl ring.[7] Recent spectroscopic and electrochemical studies of *trans*-PhCW-(dmpe)$_2$Br gave a picture of the HOMO as mostly metal-based and the LUMO as being antibonding with significant carbyne carbon character.[4b]

For [PhCOs(NH$_3$)$_5$]$^{3+}$, the higher energy absorption region at 292 nm involves substantial π to π^* character since replacement of the phenyl by an aliphatic moiety in the complex[3b] [CH$_3$C(O)CH$_2$CH$_2$COs(NH$_3$)$_5$]$^{3+}$ results in a substantial decrease of intensity. We note that this electronic structural assignment is similar to that reported previously for some other PhCW complexes[4c] and complexes containing W−chalcogen multiple bonds.[4d,e]

Excitation of [PhCOs(NH$_3$)$_5$]$^{3+}$ at 462 nm in CH$_3$CN gives rise to a broad emission centered at 632 nm with a lifetime of 55 ns. The low-temperature (77 K) emission spectrum in poly(methyl methacrylate) polymer shows a sharpening and a possible hint of vibronic structure.[8] That the excited state is predominantly triplet is shown by quenching with the anthracene triplet at a rate constant of 1.1×10^9 M^{-1} s^{-1} (the energy difference between the anthracene triplet and the Os excited state is 20 kcal/mol). The quantum yield of emission is concentration independent over the range 1×10^{-4} M to 5×10^{-4} M but is wavelength dependent; for example, $\phi_{462} = (3.5 \pm 0.2) \times 10^{-3}$, $\phi_{490} = (4.5 \pm 0.2) \times 10^{-3}$, and $\phi_{510} = (5.5 \pm 0.2) \times 10^{-3}$. This observation suggests that not all of the excited states being populated are communicating effectively, possibly due to variations in triplet character for the low-lying states. Also of interest is that ϕ_{462} for [PhCOs(ND$_3$)$_5$]$^{3+}$ is $(4.2 \pm 0.2) \times 10^{-3}$ ($\phi_H/\phi_D = 0.83$),[9] which suggests that N−H modes might be involved to some extent in nonradiative relaxation of the excited state as has been shown for Cr(III) ammines.[10] Limited support for this idea is provided by the lifetime of [PhCOs(ND$_3$)$_5$]$^{3+}$, which is found to be 62 ns in CH$_3$CN ($\tau_H/\tau_D = 0.89$).

As we have previously shown, excited states of d^2-nitridorhenium complexes are quenched by protons due to enhanced basicity at nitrogen.[2c] Although we have not observed proton-induced quenching of [PhCOs(NH$_3$)$_5$]$^{3+}$, we have found a quenching process with substituted pyridines. Table 1 summarizes our Stern−Volmer quenching data for four pyridines, which demonstrates that a correlation between k_q and the pK_a of the pyridines exists. At least four chemical mechanisms are possible for the quenching process, including (1) pyridine attack at the multiple bond in the excited state, forming a carbenium excited state cation, (2) coordination sphere expansion to yield a seven-coordinate complex, (3) π-exciplex formation in a face-to-face fashion involving the phenyl group and the pyridine, and (4) proton transfer from a coordinated amine to the pyridine. We note that both electron and energy transfer mechanisms are not energetically favorable. Proton transfer is the most probable since the bimolecular quenching rate for pyridine is extremely fast, i.e., near diffusion control (5.0×10^9 M^{-1} s^{-1}). In addition, removal of a largely metal-localized electron and transfer to an orbital with significant carbon character would render the metal center more electropositive and hence increase the acidity of the coordinated ammines. Although further studies are needed, support for a proton transfer mechanism comes from the rate of quenching of [PhCOs(ND$_3$)$_5$]$^{3+}$ by 3-fluoropyridine, which is found to be 8.2×10^6 M^{-1} s^{-1}, thus corresponding to an isotope effect of 1.10.

Table 1. Quenching of [OsCPh(NH$_3$)$_5$$^{3+}$]* with Substituted Pyridines[a,d]

	pK_a	K_{SV}[b]	k_q (M^{-1} s^{-1})
py	5.25	283	5.0×10^9
3-F-py	2.90	5.2	9.1×10^7
3-Cl-py	2.84	3.3	5.8×10^7
4-CN-py[c]	1.90	<0.06	$<10^6$

[a] As the trifluoromethanesulfonate salt in deoxygenated CH$_3$CN. [b] Stern−Volmer quenching constant using τ = 55 ns. [c] Very slight quenching observed. [d] pK_a data are taken from: *Lange's Handbook of Chemistry*, 4th ed.; McGraw-Hill: New York, 1992. *Handbook of Chemistry and Physics*, 67th ed.; CRC Press: Boca Raton, FL, 1986−1987.

In summary, it is clear that the photochemistry and photophysics of metal carbyne chromophores, especially in coordination spheres of "simple" ligands such as ammines, have a wide landscape still waiting to be explored. Current work involving the base-induced quenching mechanism of the excited state is underway as well as molecular orbital calculations that will more clearly delineate excited state structure and reactivity.

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(8) Vibronic structure has been observed in the case of *trans*-PhCW-(dmpe)$_2$Br with an average spacing of ca. 1150 cm^{-1} (see ref 4b).

(9) [PhCOs(NH$_3$)$_5$](O$_3$SCF$_3$)$_3$ was prepared by room-temperature exchange of protons in acidic D$_2$O for the precursor complex [Os(NH$_3$)$_5$(PhCH-(OMe)$_2$)]$^{2+}$, followed by preparation of the carbyne by the published procedure.[3] Deuteration was confirmed by the absence of NH$_3$ resonances in the proton NMR spectrum.

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