Charge Transfer Complexation of Ruthenium Tris-bipyridine by a Stable Carbene

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Dedicated to Professor Henning Lund on the occasion of his 70th birthday.

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A stable carbene (1) interacts strongly with $[Ru(bpy)_3]^{2+}$ to form a paramagnetic charge transfer complex, which reverts to its components upon treatment with air. Absorption spectra and cyclic voltammetric studies confirm that carbene 1 reduces to $[Ru(bpy)_3]^{2+}$ to a lower oxidation level in the complex.

By their nature, carbenes are electron deficient and therefore electrophilic, although nucleophilic carbenes have been predicted, and later trapped, by Wanzlick and co-workers.[1–4] It was not until 1991 that the first stable nucleophilic carbene was successfully isolated by Arduengo et al.[5] A variety of 'stable carbenes,' so-called because of their extraordinary stability in the absence of oxygen and moisture, have since been prepared,[6–12] although little is known about their electrochemical properties or their tendency to participate in ground or excited state electron transfer reactions.

The range of typical organic reactivity of the stable carbenes has been explored only modestly so far, although they do function as complexing ligands to transition metals.[13–18] Both the complex and the uncomplexed ligand are largely nucleophilic.[19] Enders et al.[20,21] have shown, for example, that a stable triazol-5-ylidene reacts as a typical carbene, inserting into X–H bonds (X = O, N, S) and adding to activated double bonds. The electrochemical reduction of one such stable carbene has been reported,[22] and the possibility that these stable carbenes might function as useful catalysts[23] has spurred great interest in their further characterization. The imidazol-2-ylidene carbenes 1, on the other hand, do not react comparably. Although they may differ significantly from transient, highly reactive carbenes, their stability allows for more thorough characterization by spectroscopy than is possible for their highly reactive cousins.

We here report a study on the chemical reactivity of a stable carbene 1 in the imidazol-2-ylidene series which reduces $Ru(bpy)_3^{2+}$ readily. We provide evidence for formation of a contact charge transfer complex, the first such example, to our knowledge, describing the chemical oxidation of a stable carbene.
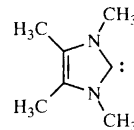
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Experimental

Solvents and materials. Tetrahydrofuran (THF, Aldrich, reagent grade) and toluene were distilled from Na–benzophenone prior to use and stored in a dry box. Acetonitrile (CH_3CN, B&J), THF (Aldrich, spectrophotometric grade), dimethyl sulfoxide (DMSO, Aldrich, spectrophotometric grade) were stored in the dry box. $Ru(bpy)_3Cl_3$, $Ru(bpy)_2Cl_2$, N,N-dimethylthiourea, 3-hydroxy-2-butanone, 1-hexanol, and potassium were used without further purification. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was recrystallized twice before being used as the electrolyte. 1,3,4,5-Tetramethylimidazol-2-ylidene (1) was prepared according to the method of Kuhn et al.[24]

All reactions and manipulations were carried out under an inert atmosphere, either in a Vacuum Atmospheres HE Dri-Lab glovebox or by using standard Schlenk techniques.

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Results and discussion

Absorption and fluorescence spectra. Carbene 1 absorbs strongly at 270 nm in DMSO and exhibits a weak band at about 350 nm that disappears upon exposure to air, Fig. 1. Nucleophilic carbenes have been reported to react with chalcogens such as oxygen, sulfur, selenium, and tellurium,[2,21,25,26] and Wanzlick *et al.*[3] have also noted a decomposition pathway for imidazol-2-ylidenes involving water and oxygen.

The carbene also shows weak fluoresecence at about 460 nm, Fig. 2. The emission band is quenched by addition of metal salts, completely disappearing, for example, when a 1 : 1 ratio of carbene-to-Cu^{2+} (Fig. 2) is attained. With mercury (Hg^{2+} as acetate), the band remains unshifted, Fig. 3, in contrast with the quenching with copper, where a red-shift of about 10 nm accompanies the quenching. With Fe^{2+} or Eu^{3+}, the carbene complex precipitates immediately.

The character of the complexation is more readily established in the complex formed by treating carbene 1 with $[Ru(bpy)_3]^{2+}$. The absorption spectrum of $[Ru(bpy)_3]Cl_2$ is characterized by an intense ligand-

Fig. 3. Emission spectra of a 4.0 mM solution of carbene **1** in deaerated THF with increasing amounts of $Hg(OAc)_2$: (1) 0; (2) 0.64 mM; (3) 1.6 mM; (4) 4.0 mM Hg^{2+}. Excitation: 345 nm.

centered $\pi-\pi^*$ transition at 290 nm and a broad metal-to-ligand charge transfer (MLCT) $d-\pi^*$ transition centered at 450 nm.[27] When carbene 1 is added to a solution of $[Ru(bpy)_3]^{2+}$, a new band appears between 500–550 nm (Fig. 4), together with a drastic increase in the absorption at 350 nm. This band cannot be attributed to a superposition of the separate absorptions of the carbene and $[Ru(bpy)_3]^{2+}$. Instead, the new spectrum is very similar to that reported in the electroreduction of $[Ru(bpy)_3]^{2+}$, successively to $[Ru(bpy)_3]^{1+}$, $[Ru(bpy)_3]^0$, and $[Ru(bpy)_3]^{1-}$.[28-30] Heath *et al.*[30,31] have assigned the two new bands (at 350 nm and 525 nm, respectively) to ligand-localized $\pi-\pi^*$ transitions. $[Ru(bpy)_3]^{1+}$ and $[Ru(bpy)_3]^0$ are strong reducing agents,[29,30] and a rapid reaction is known to take place between $[Ru(bpy)_3]^{1+}$ and O_2, quantitatively regenerating $[Ru(bpy)_3]^{2+}$.[28] Upon exposure of the mixture to air, this new band disappears and the characteristic absorption band of $[Ru(bpy)_3]^{2+}$ at 450 nm reappears (Fig. 4d), as the band at 350 nm disappears. These absorption spectra suggest that carbene 1 reduces $[Ru(bpy)_3]^{2+}$ to a more active intermediate
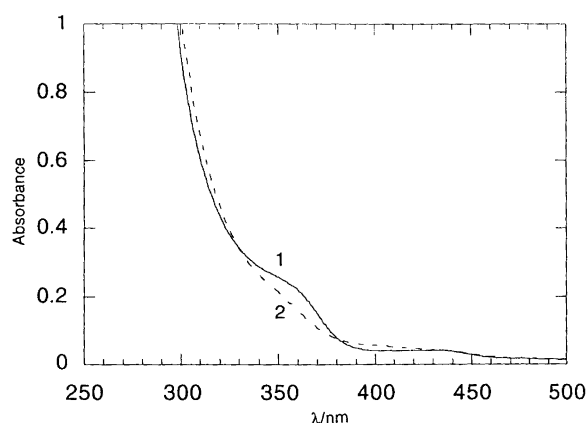
Fig. 1. Absorption spectra of 5.4 mM carbene **1** in deaerated acetonitrile before (1) and after (2) exposure to air.
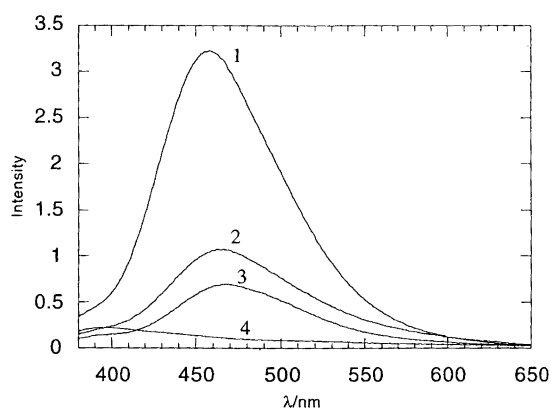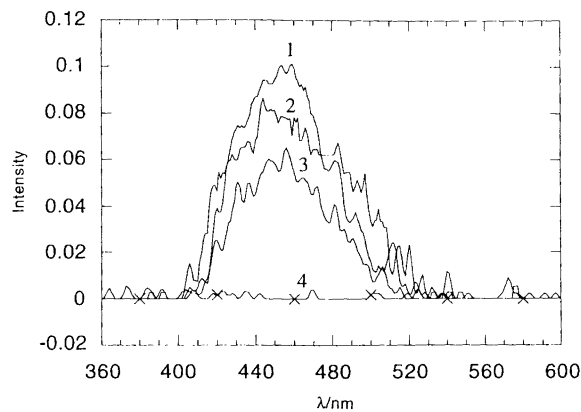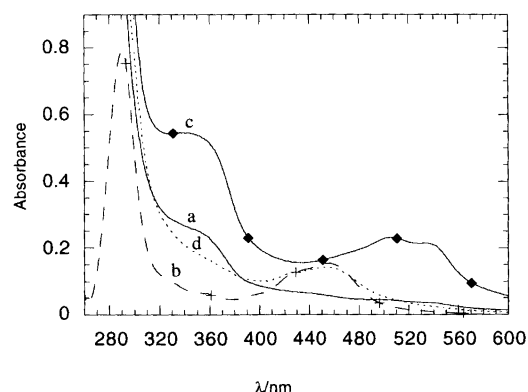
Fig. 2. Emission spectra of a 2.7 mM solution of carbene **1** in deaerated THF with increasing amounts of $CuCl_2$. (1) No Cu^{2+}; Carbene-to-Cu^{2+} ratio: (2) 10:1; (3) 5:1; (4) 1:1. Excitation: 345 nm.

Fig. 4. Absorption spectra in deaerated DMSO of: (a) 1.4 mM carbene **1**; (b) 0.05 mM $[Ru(bpy)_3]^{2+}$; (c) mixture containing 1.4 mM carbene **1** and 0.05 mM $[Ru(bpy)_3]^{2+}$; and (d) sample c after treatment of air.
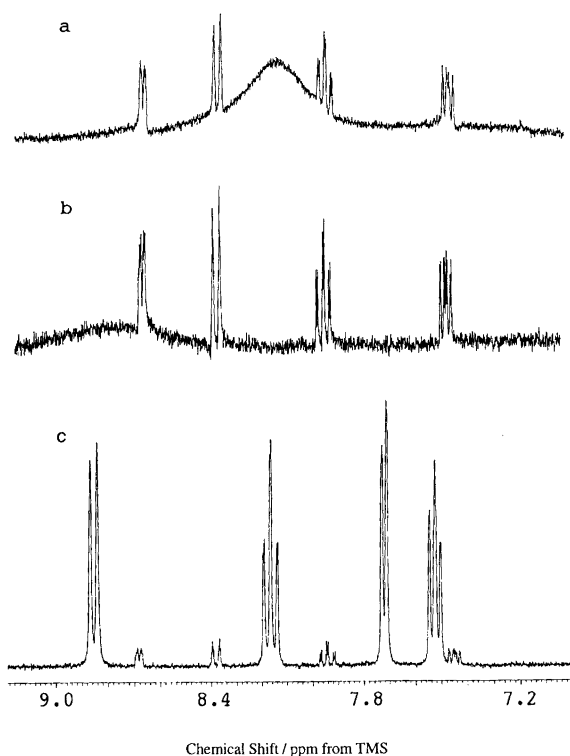
Fig. 5. ^1H NMR spectra of a 0.05 mM solution in deaerated DMSO-d_6 of: (a) and (b) carbene **1** containing $[Ru(bpy)_3]^{2+}$ with a carbene 1-to-$[Ru(bpy)_3]^{2+}$ ratio of (a) 0.5:1; and (b) 1:1; and (c) $[Ru(bpy)_3]^{2+}$ containing 15% 2,2'-bipyridine.

Fig. 6. Cyclic voltammograms in deaerated CH_3CN containing 0.1 M Bu_4NPF_6 of: (a) 2.0 mM carbene **1**; (b) 0.8 mM $[Ru(bpy)_3]Cl_2$; and (c) a mixture of 0.8 mM $[Ru(bpy)_3]Cl_2$ and 1.6 mM carbene **1**. Scan rate: 1 V s^{-1}.

$([Ru(bpy)_3]^+$ or $[Ru(bpy)_3]^0)$, which is reoxidized by O_2 to $[Ru(bpy)_3]^{2+}$, freeing the carbene which is oxidatively degraded by oxygen.

NMR spectra. The complexation can also be followed by nuclear magnetic resonance spectroscopy (NMR). ^1H NMR spectra[32] for 2,2'-bipyridine as a free ligand (bpy) and as complexed to ruthenium^{2+} $[Ru(bpy)_3]^{2+}$ are easily distinguished because they exhibit different splitting patterns and chemical shifts in the aromatic region, Fig. 5.

The changes induced in this region by treatment of a sample of carbene **1** with a fixed $[Ru(bpy)_3]^{2+}$ concentration (and containing the free bpy impurity shown in Fig. 5), but with different $[Ru(bpy)_3]^{2+}$-to-carbene **1** molar ratios ranging from 2:1 to 1:2.7, are shown in Fig. 6. In the deaerated samples, the $[Ru(bpy)_3]^{2+}$ signals at δ 7.52, 7.72, 8.17, and 8.85 have disappeared, being replaced by a broad unresolved signal centered at about 8.3. Those signals from the bpy impurity also remain. When this ratio is decreased to 1:1, this signal is shifted and broadened further; and with a 1:2.7 ratio, the broad signal disappeared completely. The aliphatic regions of all three samples are too complex to interpret.

When the latter sample is treated with air, the peaks assigned to $[Ru(bpy)_3]^{2+}$ reappear, but the aliphatic peaks assigned to the carbene have become too complex for interpretation. They do duplicate however the complexity attained if the carbene alone is treated with air.
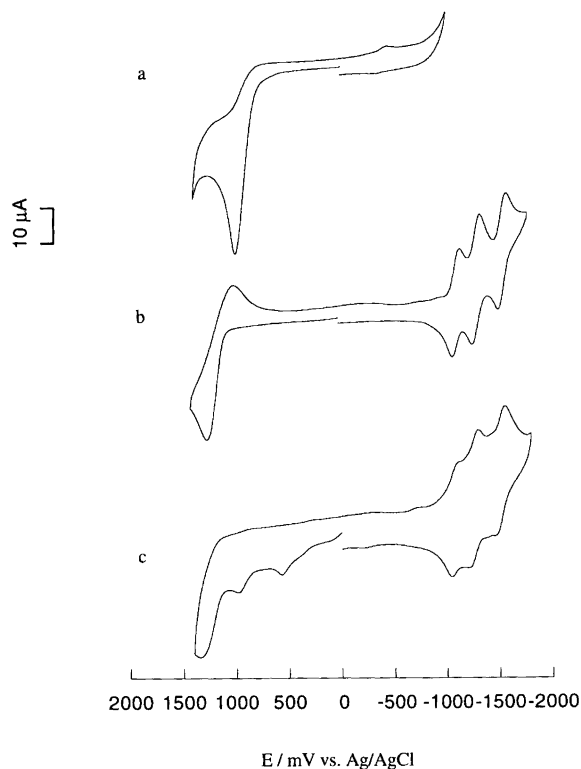
Thus, the paramagnetic species responsible for the broadened signals in the deaerated sample is destroyed by air as $[Ru(bpy)_3]^{2+}$ is regenerated.[33] Since an electron spin has a magnetic moment that is 657 times greater than that of a proton, it provides a relaxation pathway that is 500 000 times more efficient than by a proton. Therefore, significant broadening of the ^1H NMR spectrum would be expected in a charge transfer complex produced by electron donation from the carbene to the metal complex. In fact, sometimes the relaxation is so fast that the signals cannot be detected. We conclude that a 1:1 charge transfer complex is formed between $[Ru(bpy)_3]^{2+}$ and carbene **1**, producing a paramagnetic species whose NMR spectrum disappears only to be restored upon exposure of O_2.

Cyclic voltammetry. Fig. 7 is a cyclic voltammogram for carbene **1** in deaerated acetonitrile. One irreversible oxidation peak is observed at 1.0 V (vs. Ag/AgCl), suggesting that carbene **1** is capable of losing one electron to produce a radical cation, which undergoes a fast chemical reaction. No reverse reduction peak can be observed, irrespective of scan rate up to 100 V s^{-1}. After contact with air, the oxidation peak disappears, indicating that carbene **1** has decomposed.

A cyclic voltammogram for $[Ru(bpy)_3]^{2+}$, Fig. 6b, exhibits three reversible ligand-centered reduction peaks, corresponding to $[Ru(bpy)_3]^{2+}/[Ru(bpy)_3]^+$,

$[Ru(bpy)_3]^+/[Ru(bpy)_3]^0$, and $[Ru(bpy)_3]^0/$ $[Ru(bpy)_3]^-$ respectively, and one quasi-reversible metal-centered oxidation peak (Ru^{3+}/Ru^{2+}). Spectroscopic and electrochemical studies[29,30,32,34-39] have shown that the extra electron density in $[Ru(bpy)_3]^{2+}$ and like complexes are carried by the ligands and that the orbitals of the ligands that accept electrons are spatially isolated, i.e., electrons enter the π^* orbitals of the three bpy ligands of $[Ru(bpy)_3]^{2+}$ successively without delocalization when it is reduced by one, two, or three electrons, respectively. The reduced forms of $[Ru(bpy)_3]^{2+}$ would, therefore, better be expressed as $[Ru^{II}(bpy)_2(bpy^-)]^+$, $[Ru^{II}(bpy)(bpy^-)_2]^0$, and $[Ru^{II}(bpy^-)_3]^-$, respectively, all of which are paramagnetic. When carbene 1 is added to a solution of $[Ru(bpy)_3]^{2+}$, Fig. 6c, the three reduction peaks are still observed at roughly the same potentials. The fact that $[Ru(bpy)_3]^{2+}$ disappears in the absorption spectrum and ^1H NMR spectrum, upon complexation with carbene 1 but is still observed by cyclic voltammetry strongly supports the assertion that carbene 1 reduces $[Ru(bpy)_3]^{2+}$ to a paramagnetic intermediate that can be reoxidized to $[Ru(bpy)_3]^{2+}$, electrochemically or by oxygen.

Perhaps counter-intuitively, the reaction between $Ru(bpy)_2Cl_2$ and carbene 1 failed to produce analogous effects. Indeed, both the absorption spectrum and the ^1H NMR spectrum of the mixture (not included) show simple superposition of the components, indicating that no redox or any other reactions transpire between them at all. This observation can be rationalized by the reduction potential of the complex: it is known that replacement of one of the bpy ligands by a halide shifts the reduction potentials negatively, making it much more difficult to reduce than $[Ru(bpy)_3]^{2+}$.

Conclusions

Carbene 1 reduces $[Ru(bpy)_3]^{2+}$ readily at room temperature, generating a paramagnetic ruthenium tris-bipyridine complex. Oxygen reoxidizes the reduced intermediate and regenerates $[Ru(bpy)_3]^{2+}$. This is the first example of redox chemistry between a metal complex and a stable nucleophilic carbene.

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