Controlling Electronic Communication in Ethynylated-Polypyridine Metal Complexes**

Abdelkhrim El-ghayoury, Anthony Harriman,* Abderrahim Khatyr, and Raymond Ziessel*

Dedicated to Professor Jean-Marie Lehn on the occasion of his 60th birthday

The design of photoactive, molecular-scale devices is a topical subject that has led to detailed examination of numerous elaborate supermolecules. An important, and unresolved, issue concerns how best to interlock the various components into an ordered array that permits controlled transfer of stored information along the molecular axis. In principle, this problem can be overcome by careful manipulation of the energetics of the photoactive terminals and of the connecting framework, provided information transfer occurs by a superexchange mechanism.[1] Earlier work has shown that this latter requisite is met for intramolecular triplet energy transfer within alkynylene-bridged metal polypyridine complexes.[2] Indeed, extremely fast electron exchange occurs from a triplet-excited ruthenium(II) bis(2,2′:6′,2″-terpyridine) (Ru-terpy) terminal to a corresponding osmium(II)[3] or iron(II) terminal[4] along a polyalkynylene bridge, with the rate of transfer being almost insensitive to the length of the connector. This situation is ideal for rapid transfer but inappropriate for leaking information at a required rate. Other studies have shown, however, that the electronic conductivity of polyalkynes can be modulated by incorporating aromatic units in the carbon chain.[5] We have now adopted this strategy as a means to build photoactive dyads possessing similar geometries but displaying disparate rates of intramolecular electron exchange.

For a chromophore to support slow electron exchange it must possess a long-lived excited state. Thus, the triplet lifetime ($\tau_T = 0.6$ ns) of $[Ru(terpy)_2]^{2+}$ in deoxygenated acetonitrile at 20 °C is too short for the chromophore to participate in electron-exchange reactions unless the reactants are closely coupled, and the luminescence quantum yield (Φ_L) is very low. Interconnection of two such Ru-terpy units through a butadiynylene bridge,[6] giving **RR1**, extends the triplet lifetime to 720 ns, thereby allowing slow electron transfer to compete with nonradiative deactivation, and raises the emission probability (Table 1). Insertion of a phenyl ring at the center of the butadiynylene bridge,[7] giving **RR2**, shortens the triplet lifetime, reduces the emission probability, and raises the triplet energy (E_T), although the photophysical properties remain vastly superior to those of the parent. This is because of a mismatch in the energy and spatial distribution of LUMOs on the alkyne and phenyl units, which curtails extended delocalization of the promoted electron. Functionalization of the phenyl ring with 2,5-dialkoxy groups (**RR3**) causes a small increase in both triplet lifetime and emission quantum yield, while slightly lowering the triplet energy (Table 1). Replacing the phenyl ring with a naphthalene residue, forming **RR4**, prolongs the triplet lifetime to 475 ns,

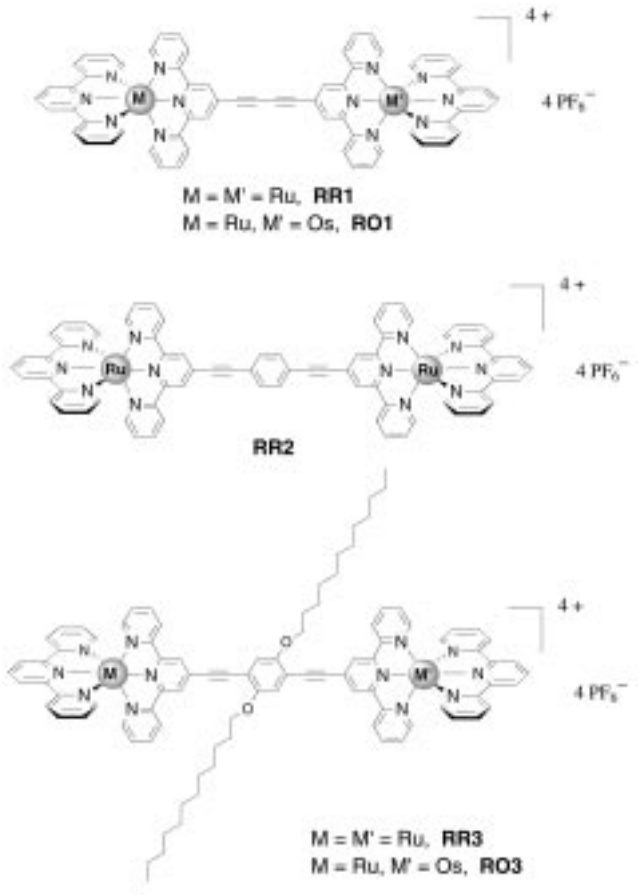

Table 1. Photophysical properties recorded for the metallo-fragments present in the various ruthenium(II) polypyridine complexes in deoxygenated acetonitrile at 20 °C.

Compd	λ_L [nm][a]	Φ_L[b]	τ_T [ns][c]	E_T [cm^{-1}][d]
$[Ru(terpy)_2]^{2+}$	650	< 0.0001	0.6	16280
RR1	735	0.0023	720	14600
RR2	685	0.0026	110	15400
RR3	693	0.0028	135	15230
RR4	702	0.0040	475	15050
R4	696	0.0035	415	15220
$[Ru(bpy)_3]^{2+}$	627	0.062	980	16950
RR5	653	0.050	820	16570
RR6[e]	661	0.050	6700	16320

[a] Emission maximum derived by spectral curve fitting, ±2 nm. [b] Emission quantum yield, ±8%. [c] Triplet lifetime, ±5%. [d] Triplet energy derived by spectral curve fitting, ±50 cm^{-1}. [e] Refers to the "Ru(bpy)" fragment since the triplet state localized on the naphthalene-based connector ($E_T = 16100$ cm^{-1}) does not emit under these conditions but shares a common lifetime ($\tau_T = 6.7$ μs).

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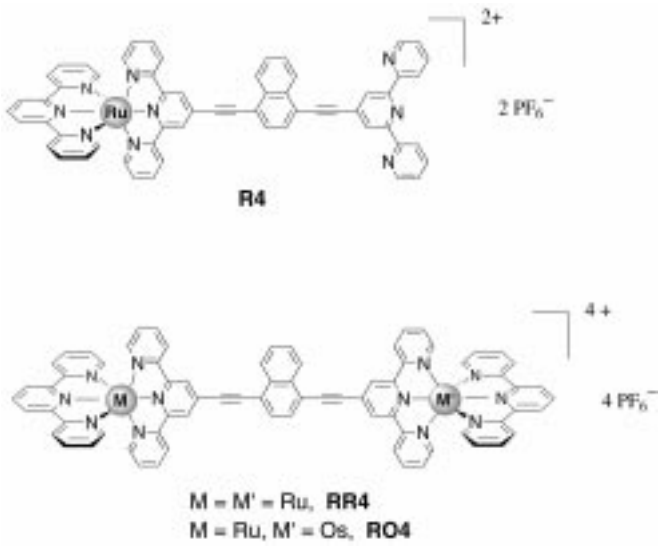


due to improved blending of the relevant LUMOs, and raises the emission probability (Table 1). The problems associated with the central phenyl ring are thereby overcome and the photophysical properties of **RR4** are almost as attractive as those of **RR1**, with the added benefit that the central unit can now be derivatized.

The triplet decay profile recorded for **RR4** in deoxygenated acetonitrile following excitation with a 10-ns laser pulse at 532 nm is mono-exponential at low laser intensity, but becomes dual-exponential as the laser intensity is increased (Figure 1). The shorter lived component has a lifetime of

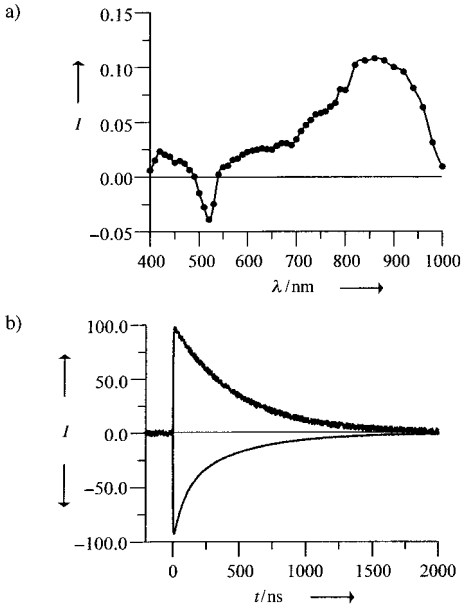
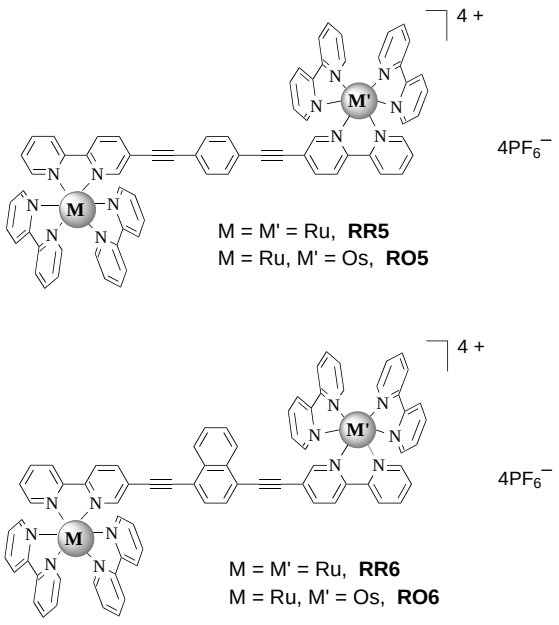


Figure 1. a) Differential absorption spectrum recorded for the triplet excited state of **RR4** in deoxygenated acetonitrile at 20 °C. The intense bleaching seen around 510 nm indicates that the triplet state is localized on the Ru-terpy chromophore. The spectral profile remains independent of laser intensity. b) Decay profiles of **RR4** recorded at 700 nm following excitation at low (upper trace) and high laser intensity (lower trace); the lower trace is inverted for clarity of presentation. At low power the decay curve corresponds to a single exponential component having a lifetime of 475 ns. The profile recorded at high power corresponds to two successive first-order (2A → A → B) processes having lifetimes of 90 and 475 ns. I = intensity.

(90 ± 5) ns, while the slower component retains a lifetime of (475 ± 15) ns. Identical decay profiles are observed by both transient absorption and time-resolved emission techniques, but decay profiles recorded for the mononuclear complex **R4** remain mono-exponential at all laser intensities. The transient absorption spectrum recorded for **RR4** (Figure 1) is independent of laser intensity. The simplest interpretation of these observations is that both Ru-terpy terminals are simultaneously promoted to the triplet state at high laser intensity, and that the shorter lived component corresponds to intramolecular triplet–triplet annihilation. The two Ru-terpy chromophores present in **RR2** and **RR3** can be simultaneously promoted to the triplet manifold, but triplet–triplet annihilation does not take place within the available time frame since decay profiles remain mono-exponential at high intensities. The effect observed with **RR4**, therefore, arises because the naphthalene-based connector both stabilizes the triplet state and promotes electron exchange on the relevant time scale. For **RR1**, it was not possible to simultaneously populate both triplet states at any laser intensity, perhaps because triplet annihilation is complete within the 10-ns laser pulse.

Relative to $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridyl), the triplet lifetime and emission probability of **RR5** are slightly reduced because of the lower triplet energy (Table 1). For the



naphthalene-bridged system **RR6**, the triplets localized on the connector ($E_T = 16\,110\ cm^{-1}$) and on the Ru-bpy terminal ($E_T = 16\,320\ cm^{-1}$) are in thermal equilibrium at room temperature, although only the metal complex emits in deoxygenated acetonitrile at 20 °C. The equilibrium mixture strongly favors the naphthalene-like triplet (75 %) and decays by first-order kinetics with a lifetime of (6.7 ± 0.2) μs in deoxygenated acetonitrile. Thus, the triplet lifetime of the Ru-bpy terminal, present in the equilibrium mixture, exceeds that of $[Ru(bpy)_3]^{2+}$ by a factor of about seven.

In the butadiynylene-linked mixed-metal complex **RO1** intramolecular triplet energy transfer (i.e., Ru → Os) is very

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fast,[3] occuring with a rate constant k_{ET} of $3.7 \times 10^{10}\ s^{-1}$ in deoxygenated acetonitrile at 20 °C. Insertion of a central phenyl ring, as in **RO3**, lowers this rate constant by a factor of about 300, while a central naphthalene unit, as in **RO4**, provides for a rate intermediate between these extreme values (Table 2). The average distance[8] separating the metal centers (d) varies somewhat among these compounds while the energy gap (ΔE_{TT}) between triplets localized on the Ru-terpy donor and Os-terpy acceptor[9] is relatively small. In fact, this modest energy gap, taken together with the long inherent triplet lifetime of the Os-terpy fragment, might be expected to facilitate reverse triplet energy transfer (i.e., Os →Ru) in **RO3** and **RO4**.

It is convenient to describe the rate constant for through-bond energy transfer (k_D) in terms of the Fermi golden rule [Eq. (1)],[10] where FC refers to the Franck–Condon weighted density of states and V_{DA} is the electronic coupling matrix element for electron exchange. The Franck–Condon factor can be calculated by reference to luminescence spectra recorded for the appropriate mononuclear Ru and Os complexes,[10] thereby allowing an estimation of the matrix element (Table 2). To relate k_D to the experimentally determined k_{ET} [Eq. (2)] it is necessary to allow for Förster-type coulombic energy transfer, but the rate constant for this process (k_F) is readily calculated from spectral characteristics of the relevant mononuclear complexes.[11]

$$k_D = \frac{2\pi}{\hbar} |V_{DA}|^2 FC \quad (1)$$

$$k_{ET} = k_D + k_F \quad (2)$$

The derived rates are compiled in Table 2 and indicate that, because of the poor emission characteristics of the Ru-terpy fragment, Förster-type energy transfer is negligible in these systems. As such, the derived k_{ET} values reflect the magnitude of electronic coupling between the reactants, and it is seen that the central aromatic unit imposes a severe barrier for through-bond electronic interactions. In part, this barrier arises from the extended length of the connector, but there is also a substantial difference between the value of V_{DA} derived for **RO3** and **RO4**, for which the metal–metal separation remains identical. Note the qualitative correspondence between k_{ET} for the Ru/Os complexes and τ_T measured for the binuclear Ru-terpy complexes. It is apparent that both parameters are controlled by electronic factors associated with the polyalkynylene connector.

The superexchange mechanism allows for virtual population of the triplet state localized on the connector such that V_{DA} can be expressed in the form of Equation (3),[1] where ΔE_{DS} is the energy gap between triplet states localized on the connector and donor and α is the product of atomic orbital coefficients describing coupling between 1) donor and connector, 2) successive subunits within the connector, and 3) connector triplet, and acceptor.

$$V_{DA} = \frac{\alpha^2}{\Delta E_{DS}} \quad (3)$$

The various ΔE_{DS} values are available from emission spectroscopy, thereby enabling estimation of the connectivity term α (Table 2). Coupling along the butadiynylene bridge is extremely effective, offsetting the relatively large energy gap between donor and connector, and conducive for fast electron exchange. A central aromatic unit imposes a severe drop in the degree of connectivity along the molecular axis, and this must arise because of poor electronic coupling between alkynylene and aromatic fragments, although similar α values are found for both phenylene and naphthalene spacers. The faster rate and higher value of V_{DA} found for **RO4** relative to **RO3** can now be ascribed to the relative ΔE_{DS} values, bearing in mind that the triplet energy of the naphthalene-based connector is much lower than that of the phenylene-bridged system.[12]

Again, comparison can be made with the corresponding 2,2′-bipyridyl-based systems, and it is seen that intramolecular triplet energy transfer across a central phenylene spacer is about sevenfold faster for **RO5** than for **RO3** (Table 2). This rate enhancement can be traced to the fact that both V_{DA} and α are higher for the 2,2′-bipyridyl-based system. Although there is a small difference between ΔE_{DS} values derived for these two compounds, the faster rate of energy transfer found for **RO5** stems mainly from improved blending of orbitals along the connector. The situation is more complicated for the naphthalene-bridged 2,2′-bipyridyl-based system **RO6** since energy transfer proceeds by intermediate population of the triplet localized on the connector. In fact, energy transfer from the connector triplet to the Os-bpy terminal ($k_{ET} = 1.7 \times 10^{10}\ s^{-1}$) intercepts reversible triplet energy transfer between the Ru-bpy terminal and the connector, for which both forward ($k_{ET} = 1.1 \times 10^{10}\ s^{-1}$) and reverse steps

Table 2. Parameters relating to triplet energy transfer in the various mixed-metal Ru-Os dyads, with reference to measurements made in deoxygenated acetonitrile at 20 °C.

Compd	Process[a]	k_{ET} [μs^{-1}][b]	k_F [μs^{-1}]	k_D [μs^{-1}]	ΔE_{TT} [cm^{-1}]	λ_{TT} [cm^{-1}][c]	d [Å]	FC [cm][d]	V_{DA} [cm^{-1}][e]	ΔE_{DS} [cm^{-1}]	α [cm]
RO1	Ru →Os	37000	30	37000	890	1700	15.5	4.6×10^{-5}	26.0	5670	385
RO3	Ru →Os	116	2	114	730	1400	19.8	1.3×10^{-4}	0.9	6000	70
RO4	Ru →Os	1060	1	1059	700	1400	19.8	1.2×10^{-4}	2.7	1480	65
RO5	Ru →Os	800	8	792	2995	2285	18.1	2.0×10^{-4}	2.0	5400	100
RO6	Ru →N	10900	< 1	10900	305	1455	18.1	6.6×10^{-5}	11.8	na[f]	na
RO6	N →Os	17000	< 1	17000	2335	1200	18.1	1.8×10[f]	8.9	na	na

[a] Direction of triplet energy transfer, N refers to naphthalene. [b] Experimental rate constant for electron exchange, ± 10 %. [c] Total reorganization energy accompanying triplet energy transfer, ± 100 cm^{-1}. [d] Franck–Condon weighted density of states calculated from spectroscopic properties recorded for appropriate mononuclear complexes, ± 5 %. [e] Matrix element for electron exchange, ± 10 %. [f] na = not applicable.

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($k_{ET} = 2.4 \times 10^9\ s^{-1}$) can be evaluated by time-resolved emission spectroscopy.[13]

It is instructive to compare the times required to populate the Os-based acceptor in **RO4** and **RO6** (Figure 2) as a means to assess the benefits of a two-step, energy-transfer process with respect to direct (long-range) transfer.[14] Thus, the maximum yield of the Os-terpy triplet state attainable by

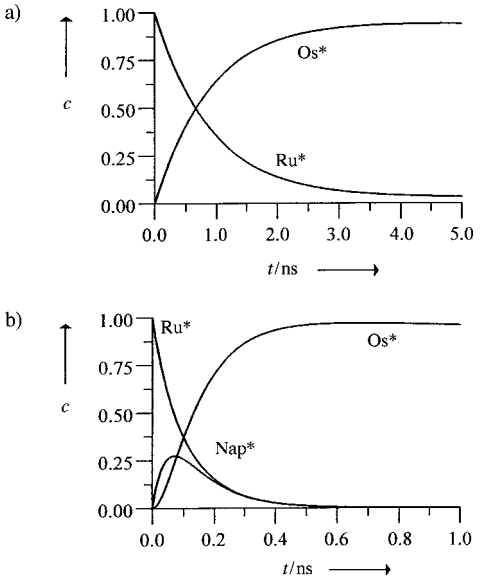

Figure 2. a) Kinetic simulation for **RO4** showing how the concentration c of triplet states localized on Ru-terpy (Ru*) and Os-terpy terminals (Os*) vary with time t following selective excitation of the Ru-terpy unit. The long tail seen in the decay of Ru* is due to reverse energy transfer from Os*. b) Corresponding simulation for **RO6** showing intermediate population of the triplet state localized on the naphthalene-based connector (Nap*). Simulations were based on the experimentally determined rate constants.

energy transfer in **RO4** corresponds to 94% of the initially populated Ru-terpy triplet and is reached after 4.8 ns. For **RO6**, the maximum yield of Os-bpy triplet is 97% and is reached after only 670 ps. The two-step mechanism, in this case, is much faster than long-range (i.e., 20 Å) transfer. This finding indicates the benefit of having an intermediary relay but also shows that, in a properly designed system, long-range energy transfer can be competitive.

Electron exchange in mixed-metal Ru/Os polypyridine complexes is an established subject. Remarkably, the fastest and the slowest rates of triplet energy transfer between terpy-based terminals have been measured for systems built around alkynylene connectors. The degree of electronic interaction between the metallo terminal and an alkyne is readily modulated by inserting an aromatic unit into the carbon chain, and this has similar effects on both the triplet lifetime and on the rate of electron exchange in binuclear complexes. An unusual effect of the alkynylene connector is that it perturbs terminal Ru-terpy and Os-terpy units to different degrees, such that the resultant triplet energy gap ΔE_{TT} becomes sufficiently small to facilitate reversible triplet energy transfer along the molecular axis. By prolonging the triplet lifetime and providing a favorable pathway for electron exchange, the diethynylated naphthalene connector permits slow energy-transfer steps to compete with nonradiative deactivation of the excited state. Thus, the first example of triplet–triplet annihilation in a ruthenium(II) polypyridine complex is described. Finally, our approach allows the triplet energy of the connector to be sited slightly above or below that of the donor. By way of **RO4** and **RO6**, this provides the first opportunity to compare long-range and successive short-range energy-transfer steps in structurally related molecular systems.

Experimental Section

All new complexes were prepared by complexation of the ditopic ligands with appropriate metal precursors; $[Ru(terpy)(dmso)Cl_2]$ (dmso = dimethyl sulfoxide) for terpy-based compounds and $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ for bpy-based complexes. The resultant complexes were purified by chromatography over alumina, followed by double recrystallization. The purity of each new compound was shown to be greater than 98% by spectroscopic and elemental analyses (see the Supporting Information for details). Photophysical measurements were made with a variety of laser excitation sources. For the symmetrical binuclear complexes, the laser excitation wavelength was 532 nm (FWHM = 25 ps or 10 ns), and triplet-state properties were monitored by both transient absorption and time-resolved emission spectroscopy. Kinetics for energy-transfer processes were established by time-correlated, single-photon counting studies following excitation with a frequency-doubled Ti-SAPPHIRE laser (FWHM = 0.3 ps). Emission from either the Ru- or Os-based chromophore was separated with a high-resolution, dual monochromator system before being sampled with a microchannel plate phototube. The time resolution of this instrument, after deconvolution of the instrumental response function, was about 25 ps. Kinetic information was also established by transient absorption spectroscopy following laser excitation at 440 nm (FWHM = 0.35 ps). All experiments were carried out in deoxygenated acetonitrile at 20 °C.

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[8] Molecular dimensions used here and in the Förster-type calculations were determined from structures simulated with computer molecular dynamics (ZINDO-S parameters) after full-energy minimization using the AMBER force field.
[9] Triplet energy levels were derived by fitting the luminescence spectra recorded for the relevant mono- or binuclear complexes at room temperature, and for the free ligands at various temperatures, to the spectral curve-fitting analysis described in ref. [10]. For more details, see A. Harriman, F. M. Romero, R. Ziessel, A. C. Benniston, *J. Phys. Chem.* **1999**, *103*, 5399.
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[11] In calculating the orientation factor it has been assumed that the lowest energy triplet states correspond to charge transfer from the metal center to the ethynylated ligand. This gives a total of 18 and 12 active transition dipoles out of the overall 36 transition dipoles for terpy- and bpy-based systems, respectively. Orientation factors and

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center-to-center distances were calculated from the computer-simulated structures, and the overlap integral, calculated from emission and absorption spectra, was assumed to contain 36 equal contributions. For more details, see V. Grosshenny, A. Harriman, M. Hissler, R. Ziessel, *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 2223.

[12] The triplet energies of the ditopic ligands used to assemble complexes **RO3** and **RO4** were derived to be 21400 and 16700 cm^{-1}, respectively, from room-temperature emission spectra recorded in micellar media. The triplet energy for the ditopic ligand present in **RO1** was found to be 20270 cm^{-1} from phosphorescence spectra recorded at 77 K. Triplet energies for the bpy-based ditopic ligands relevant to **RO5** and **RO6** were measured to be 21970 and 16100 cm^{-1}, respectively, from room-temperature emission spectra recorded in micellar media.

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[14] These values were derived from a compartmental kinetic analysis, allowing for reversible energy transfer, by solving the successive differential equations and using experimentally determined rate constants.

$[Ti(CO)_4(\eta^3\text{-}BH_4)]^-$ and $[Ti(CO)_4(\eta^5\text{-}C_4H_4N)]^-$: The First Zerovalent Metal Complexes Containing η^3-Borohydride and Pyrrolyl Ligands**

Paul J. Fischer, Victor G. Young, Jr., and John E. Ellis*

Dedicated to Professor Heinrich Nöth on the occasion of his 70th birthday

Metal borohydrides are an important class of substances that are known for practically all metals throughout the periodic table. Most contain metals in positive formal oxidation states.[1] Indeed, only two well-defined examples of zerovalent metal borohydrides have been reported, and both of these contain bidentate borohydride ligands: $[Mo(CO)_4(\eta^2\text{-}BH_4)]^-$[2] and $[Cr(CO)_4(\eta^2\text{-}BH_4)]^-$.[3a] We now report on the new zerovalent metal borohydride $[Ti(CO)_4(\eta^3\text{-}BH_4)]^-$ (**1**), the first to contain titanium and a tridentate borohydride ligand.

The synthetic route to this borohydride complex also appears to be unprecedented, that is, the reaction of $BH_3\cdot$THF with a mononuclear metal carbonyl anion.[4a] Prior reactions of this type provided only $M-BH_3$[4b] or $M-\eta^2\text{-}B_2H_5$ complexes.[5] The above-mentioned Group 6 zerovalent metal carbonyl borohydride complexes were obtained as pure products by treatment of an appropriate metal carbonyl with borohydride salts.[2, 3a] Complex **1** is is a very labile species and appears to be the most reactive isolable synthon for neutral $\{Ti(CO)_4\}$, a highly unsaturated 12-electron fragment (see below).

Treatment of a slurry of $[K([15]crown\text{-}5)_2]_2[Ti(CO)_6]$[3b] with $BH_3\cdot$THF (10 equiv, unoptimized) in THF at $-60\,^\circ C$ provided a very air-sensitive red solution. After careful separation of non-carbonyl by-products, deep red, pure, solid $[K([15]crown\text{-}5)_2]$-**1** was isolated in 38% yield (see Experimental Section) as a thermally stable substance at room temperature. By an analogous procedure [K([18]crown-6)]-**1** was obtained in 15% yield as orange-red microcrystals.[6]

Spectroscopic properties of both salts are virtually identical for the anionic component and are described here in detail for the $[K([15]crown\text{-}5)_2]^+$ salt. The IR spectra in THF show two peaks (1945(m), 1811(s) cm^{-1}) in the ν(CO) region that have the same pattern as observed for other titanium tetracarbonyl complexes in THF, including $[Ti(CO)_4(\eta^5\text{-}C_5H_5)]^-$ (**2**; $\tilde{\nu}(CO) = 1921$ (m), 1779 cm^{-1} (s)).[7a] The ν(CO) values of **1** are the highest reported for any titanium tetracarbonyl complex and suggest that $[BH_4]^-$ is the weakest donor presently known to stabilize this Ti^0 unit. The IR spectra of Nujol mulls of **1** in the ν(BH) region show bands at 2495 (m), 2132 (vw), and 2058 cm^{-1} (w), which have a pattern diagnostic of tridentate borohydride ligands.[1a] The borohydride signals observed in the ^1H ($\delta_H = -3.60$, 1:1:1:1 quartet, $J_{B,H} = 85$ Hz) and ^{11}B NMR spectra ($\delta_B = -6.42$, binomial quintet, $J_{H,B} = 87$ Hz) at 23 °C are consistent with the presence of a highly fluxional BH_4 group, as expected on the basis of prior studies.[1a] As the temperature was lowered, the 1:1:1:1 quartet in the ^1H NMR spectrum broadened and coalesced at $-63\pm5\,^\circ C$. At $-95\,^\circ C$ the slow exchange limit was reached, and two broad singlets of relative intensity 3:1 were present at $\delta_H = -4.87$ and 0.044, respectively, the weighted average of which is in satisfactory agreement with the resonance position at 23 °C. This study corroborated the presence of a η^3-BH_4 ligand in **1** and allowed the free energy of activation of the bridging/terminal hydrogen (H_t/H_b) exchange process to be calculated as 8.8 ± 0.2 kcal mol^{-1} by standard procedures.[7b] This barrier is somewhat lower than the corresponding $\Delta G^{\ddagger}$ of 10.0 ± 0.2 kcal mol^{-1} reported for $[Mo(CO)_4(\eta^2\text{-}BH_4)]^-$, the only other borohydride carbonyl complex for which this value is known.[2]

A single-crystal X-ray diffraction study on the [K(18-crown-6)]$^+$ salt confirmed the existence of **1** in the solid state.[8] Two independent anions with nearly identical structures were present in the unit cell, and that shown in Figure 1 will be described in some detail here. All hydrogen atoms of the borohydride ligand were visible in the difference map after the remaining anisotropic refinement was complete. The linear H_t-B-Ti skeleton (179(2)°), three short Ti–H distances (av 2.02(4) Å), and the associated short Ti–B distance (2.158(7) Å) are all indicative of a η^3-BH_4–Ti interaction. Slightly longer Ti–B distances in tridentate borohydride Ti^{IV} complexes have been reported, including $[Ti(OAr)_3(\eta^3\text{-}BH_4)]$ (Ar = 2,6-*i*$Pr_2C_6H_3$; 2.20(1) Å[9a]), and $[Ti(BP)_2(\eta^3\text{-}BH_4)_2]$ (BP = a biphenoxo dianion; 2.19(1) Å[9b]). The coordinated borohydride ligand is essentially tetrahedral, with an average B–H_b distance of 1.11(2) Å, which does not significantly differ

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