

Electronic Communication between Metal Centers Across Unsaturated Alkylidyne Ligands

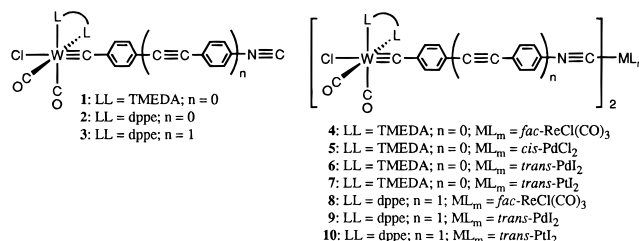
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Received July 3, 1998

Molecular systems in which metal centers are electronically coupled across unsaturated bridging ligands have been the focus of research efforts for several decades.¹ In recent years, the interest in this area of chemistry² has intensified due to general expectations that electronic communication between distant metal centers will be of importance in the quest for molecular devices and materials.³ Due to their highly covalent nature, metal–carbon π bonds have proven particularly effective in establishing electronic coupling between metal centers across unsaturated organic ligands.^{4,5} Transition-metal alkylidyne complexes^{5,6} are characterized by the presence of strong metal–carbon triple bonds, and some representatives of this class also possess the kinds of photophysical properties⁷ which are essential for the function of photochemical molecular devices.⁸ On account of this special combination of electronic and photophysical molecular properties, alkylidyne metal complexes are promising as building blocks for the design of molecular devices and materials.⁹ We are especially interested in developing systems in which the alkylidyne metal

center is connected in a conjugated manner to a remote metal center with distinctly different electronic properties.¹⁰ In this way, we are employing the isocyanide functionality¹¹ as a means of attaching additional metal centers to alkylidyne ligands.



Two series of heteronuclear metal complexes, **4–7** and **8–10**,¹² containing the 4-isocyanobenzylidyne and the 4-(4-isocyanophenyl)benzylidyne ligand were prepared by reaction of the tungsten complexes **1**¹³ and **3**¹⁴ with *fac*-ReCl(CO)₃(THF)₂, PdCl₂, PdI₂, and PtI₂ in THF solution.¹⁵ The results of the spectroscopic studies are summarized in Table 1. The palladium and platinum derivatives **5–7** as well as **9** and **10** exhibit higher IR stretching frequencies for the isocyanide groups than the rhenium complexes **4** and **8**, showing that the palladium and platinum metal complex fragments are stronger electron acceptors than the rhenium moiety.^{11a} The stretching frequencies of the tungsten-coordinated carbonyl ligands reflect the difference in electron density at tungsten between the TMEDA- and dppe-substituted complexes **1**, **4–7** and **2**, **3**, **8–10**, respectively, but they are virtually invariant within each series. Thus, if the remote metal center has any influence on the electron density at tungsten, it cannot be discerned by IR spectroscopy.

All of the complexes **1–10** exhibit two absorptions associated with the tungsten alkylidyne fragment (Figure 1a), a weak absorption at low energy and a more intensive absorption at higher energy, which are assigned to the $d_{xy} \rightarrow \pi^*_{MC}$ and the $\pi_{MC} \rightarrow \pi^*_{MC}$ transitions, respectively.^{7,16} The attachment of metal centers to the isocyanide groups of **1** and **3** causes a red-shift of both absorptions, whereby the observed influence is larger for **1** than for the extended alkylidyne complex **3**. The palladium and platinum complexes **5–7** and **9** and **10** have lower $d_{xy} \rightarrow \pi^*_{MC}$ transitions than the rhenium complexes **4** and **8**. While the energy of the tungsten d orbital remains unaffected, as shown by the IR data, the energy of the π^*_{MC} orbital seems to be lowered more by the more strongly electron-withdrawing metal complex fragments. A comparison of the data for compounds **1** and **2** furthermore shows that the energy of the $d_{xy} \rightarrow \pi^*_{MC}$ transition can be modified independently of the alkylidyne π system by ligand substitution on the metal center.

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(12) Complexes were isolated in yields of 20–73% and characterized by NMR and IR spectroscopy and elemental analysis. Complete experimental details are provided as Supporting Information.

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Table 1. Spectroscopic Data of Complexes **1–10** in CH₂Cl₂ at Room Temperature

cmpd	$\nu(\text{C}\equiv\text{N})$ (cm ⁻¹)	$\nu(\text{W}\text{C}\equiv\text{O})$ (cm ⁻¹)	$\lambda_{\text{d}\rightarrow\pi^*}$ (nm) ($\epsilon, \text{M}^{-1} \text{cm}^{-1}$)	λ_{em} (nm)	τ (μs)	$\phi_{\text{em}} \times 10^4$ ^b	$k_{\text{r}} = \phi_{\text{em}}/\tau$ $\times 10^3$
1	2124	1992, 1902	476 (560)	656	0.5	16.0	3.2
2	2124	2010, 1944	456 (590)	664	0.2	<i>a</i>	
3	2125	2006, 1940	462 (950)	680	0.7	11.4	1.6
4	2185, 2151	1992, 1904	490 (1640)	670	0.3	19.8	6.6
5	2228, 2212	1994, 1906	500 (1640)				
6	2199	1992, 1906	494 (1900)				
7	2193	1994, 1904	500 (1760)	682	0.2	14.7	7.4
8	2185, 2151	2008, 1940	464 (2980)	686	0.6	9.4	1.6
9	2201	2008, 1940	470 (3050)	685	0.1	1.9	1.9
10	2197	2006, 1942	470 (3130)	685	0.6	9.0	1.5

^a Not measured. ^b [Ru(bpy)₃]Cl₂ in deionized water is used as reference, and all samples are irradiated at 453 nm. The luminescence quantum yield of the reference is 0.055 with irradiation at 453 nm.²³

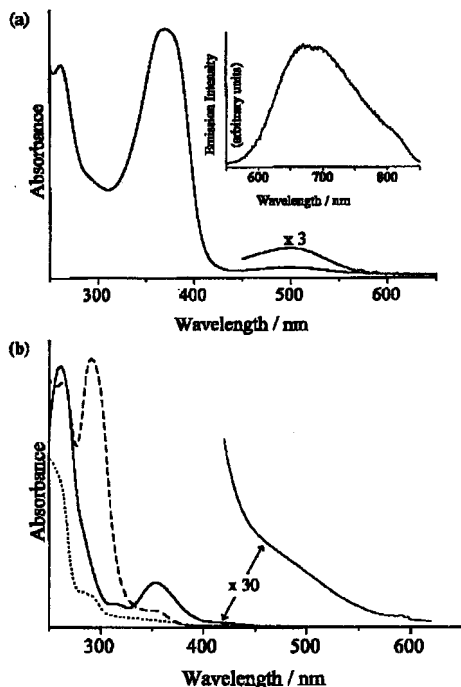


Figure 1. (a) Absorption spectrum of **7** in CH₂Cl₂ solution. The uncorrected fluorescence emission spectrum of **7** in deaerated CH₂Cl₂ solution is shown in the inset. (b) Absorption spectra of **12** (···), **13** (—), and **14** (---) in CH₂Cl₂ solution ($\sim 8 \times 10^{-6}$ M). the absorption tail of **13** is enlarged for clarity.

All tungsten benzylidene complexes **1–10**, except the palladium derivatives **5** and **6**, luminesce at room temperature in fluid solution upon excitation of the $d_{xy} \rightarrow \pi^*_{\text{MC}}$ transition (Figure 1a, inset). The emission of **1** is red-shifted significantly upon coordination of metal centers to the isocyanide group, while the emission of **3** is only modestly affected by the attached metal centers. The emission intensity is very sensitive to the nature of the isocyanide metal complex fragment. In particular, the complete quenching of the emission of the tungsten fragments in **5** and **6** by the palladium moieties is striking. In contrast to **6**, the extended palladium alkylidene complex **9** is weakly emissive.

To elucidate the reason for the nonemissive behavior of **5** and **6**, we prepared the isocyanide metal complexes $\text{ML}_m(\text{CNC}_6\text{H}_3\text{-}i\text{-Pr}_2\text{-}2,6)_2$, **11** ($\text{ML}_m = \text{fac-ReCl}(\text{CO})_3$), **12** ($\text{ML}_m = \text{cis-PdCl}_2$), **13** ($\text{ML}_m = \text{trans-PdI}_2$), and **14** ($\text{ML}_m = \text{trans-PtI}_2$) as model systems for the metal bis-isocyanide metal cores of the complexes **4–10** and determined their spectroscopic¹⁷ and electrochemical¹⁸ parameters. It was found that in the complexes **11–14**, there are no absorption bands in the region where the $d_{xy} \rightarrow \pi^*_{\text{MC}}$ transitions of the complexes **4–10** occur (Figure 1b). Only the palladium complex **13** exhibits a long tail of absorption with very low intensity which extends toward 600 nm. Thus in the low-energy

spectral region, the absorption of light is almost exclusively due to the tungsten-centered $d_{xy} \rightarrow \pi^*_{\text{MC}}$ transition. It has also been determined that the complexes **11–14** are completely nonemissive. Thus, the emissions can be attributed exclusively to the tungsten alkylidene fragments. Because of the existence of an absorption tail of very low intensity in the $\text{PdI}_2(\text{CNAr})_2$ moiety, which overlaps slightly with the expected emission of the tungsten benzylidene fragment, there exists the possibility of the presence of a low-lying ligand-field triplet state¹⁹ in the palladium moiety which deactivates the excited states in **6** and **9** via energy transfer. However, this is not the case with **5**, for which the absorption tail is blue-shifted (Figure 1b), as expected from ligand-field considerations.¹⁹ Furthermore, the electrochemical data show that the quenching of the excited state via internal electron transfer is a favorable process for **5**, as well as for **6** and **9**.²⁰ Thus, for the palladium dichloride derivative **5**, internal electron transfer is the *only* reasonable quenching mechanism.²¹ It would appear likely that electron transfer is also the active quenching mechanism in the palladium diiodide complexes **6** and **9**.

In summary, unsaturated isocyanidealkylidynes have been established as ligands for extended α,ω -dimetalla- π -systems.²² In appropriate cases, vectorial photoinduced electron transfer from the metal alkylidene fragment to the isocyanide-coordinated metal can be achieved, and, at least in principle, the possibility for energy transfer exists.

Acknowledgment. Support of this work by the Hong Kong Research Grants Council and the Committee on Research and Conference Grants of the University of Hong Kong is gratefully acknowledged. M.P.Y. Yu acknowledges the receipt of a Postgraduate Studentship, administered by The University of Hong Kong. We thank Professor Harry B. Gray and Dr. Vincent M. Miskowski for helpful discussions. This paper is dedicated to Professor Helmut Werner on the occasion of his 65th birthday.

Supporting Information Available: Experimental procedures and characterization data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA982324H

(17) $\lambda_{\text{max}}/\text{nm}$ (CH₂Cl₂, $\epsilon/\text{M}^{-1} \text{cm}^{-1}$): **11**: 344 (4290 sh), 326 (8410 sh), 310 (10500 sh); **12**: 320 (1350), 284 (6440 sh); **13**: 500 (60 sh), 402 (1390 sh), 354 (10700), 262 (72300); **14**: 422 (100 sh), 352 (2000), 292 (30600).

(18) For complexes **11–14**, the following irreversible reduction waves are observed; E_{pc} (THF, V vs SCE): **11**: -1.866; **12**: -1.150; **13**: -1.143; **14**: -1.503.

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(20) The oxidation potential of the excited metal alkylidene fragment (W) can be estimated as follows: $E(W^+/W^*) = E(W^+/W^0) - E_{0-0} = -1.258$ V vs SCE. For an oxidative quenching reaction, $\Delta E = E(\text{Ox}/\text{Ox}^-) - E(W^+/W^*)$, whereby Ox denotes the metal complex fragments **11–14**. For the palladium complexes, $\Delta E > 0$. However, for the rhenium and platinum complexes, $\Delta E < 0$.

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