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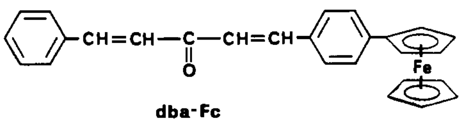
Communications

Binuclear Compounds Containing Pendant Electroactive Groups: Photophysical and Electrochemical Properties of Tris(4-ferrocenyldibenzylideneacetone)dipalladium(0), $Pd_2((C_5H_5)Fe(C_5H_4)(C_6H_4)CHCH(CO)CHCHC_6H_5)_3$

There has been increasing interest in organometallic complexes having pendant redox-active ligands, particularly complexes in which changing the oxidation state of a pendant ligand affects both the spectroscopic properties and the reactivities of the metal centers without altering the coordination sphere.[1,2] These changes in spectroscopic properties and reactivities are often related to electronic and steric effects, and one may thus visualize using the redox properties of a pendant ligand to tune the electron density at the metal centers of a complex as a potential means for rational control of reactivity. Although this simple methodology has been applied to the ground-state chemistry of organometallic complexes,[1,2] the possibility of tuning photochemical reactivity via changes of oxidation state of pendant redox-active ligands has not yet been explored.

We now wish to report the characterization and properties of a binuclear palladium(0) complex, Pd_2(dba-Fc)$_3$ (dba-Fc = 4-ferrocenyldibenzylideneacetone), which contains a new bridging ligand derived from ferrocene (structure I).



dba-Fc

I

We chose this ferrocene-based ligand because the ferrocene-centered oxidation is reversible[3] and the lowest excited states for ferrocene (and its substituted derivatives) and its oxidized form, the ferrocenium ion, are well characterized.[4] The Pd_2 species was selected because the synthetic chemistry is simple,[5] the UV-visible spectra have already been interpreted,[6] and the complexes are luminescent, which permits easy study of the excited states.[7]

The UV-visible spectrum of Pd_2(dba-Fc)$_3$[8-10] is very similar to that of Pd_2(dba)$_3$ (Figure 1), for which band assignments have previously been made.[6] The MLCT (17 850 cm^{-1}; ϵ = 14 600 M^{-1} cm^{-1}), $p\sigma \leftarrow d\sigma^*$ (25 000 cm^{-1}; 25 600 M^{-1} cm^{-1}) and intraligand (29 400 cm^{-1}; 50 300 M^{-1} cm^{-1}) transitions of Pd_2(dba-Fc)$_3$ are assigned on the basis of their frequencies, absorptivities, and band shapes. The ferrocenyl-localized ligand field band (LF)[4] is located at 20 830 cm^{-1} for free dba-Fc (ϵ = 4330 M^{-1} cm^{-1}; THF solution) but is not apparent in the Pd_2(dba-Fc)$_3$ spectra, presumably due to the stronger absorptivities of the MLCT and $p\sigma \leftarrow d\sigma^*$ bands. Nonetheless, the lowest singlet excited state is an MLCT state.

Pd_2(dba-Fc)$_3$ is weakly luminescent at 77 K (2-MeTHF solution; τ_e = 0.36 μs,[11] Φ_e = 0.0068[12]). For comparison purposes, τ_e (8.3 μs) and Φ_e (0.34) have also been measured for Pd_2(dba)$_3$, and the radative ($k_r = \Phi_e/\tau_e$) and non-radiative ($k_{nr} = (1 - \Phi_e)/\tau_e$) rate constants are listed in Table I. Ferrocenyl substitution affects both k_r and k_{nr}, with k_r decreasing by a factor fo 2 while k_{nr} increases 35-fold. Ferrocene and its derivatives are known to be efficient triplet-excited-state quenchers via energy-transfer processes (E_T(ferrocene) ~ 15 000 cm^{-1}),[13] and the presence of

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(6) Harvey, P. D.; Adar, F.; Gray, M. B. *J. Am. Chem. Soc.* **1989**, *111*, 1312.

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(8) (a) Dba-Fc was prepared according to a procedure reported elsewhere: Harvey, P. D.; Gan, L.; Aubry, C. *Can. J. Chem.* **1990**, *68*, 2278. (b) Pd_2(dba-Fc)$_3$ was prepared according to standard procedures outlined for the M_2(dba)$_3$ complexes (M = Pd, Pt).[5]

(9) (a) The Pd_2(dba-Fc)$_3$ ^{1}H NMR spectra show complex patterns similar to those reported for the M_2(dba)$_3$ complexes.[9b-d] The added complexity in the ferrocenylic proton range (CDCl$_3$, δ_{ppm} = 4.10 m (5 H), 4.41 m (2 H), 4.65 m (2 H)) indicates that more than one conformational isomer exists. (b) Keasey, A.; Mann, B. E.; Yates, A.; Maitlis, P. M. *J. Organomet. Chem.* **1978**, *152*, 117. (c) Ukai, T.; Kawazura, H.; Ishil, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253. (d) Tanaka, H.; Kawazura, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2815, and references therein.

(10) (a) The Pd_2(dba-Fc)$_3$ FT-IR[10b] and FT-Raman[10c] spectra exhibit ν(PdC) at 287 (IR), 320 (IR, R) and 352 cm^{-1} (R). These values can be compared with those for Pd_2(dba)$_3$ (287 (R), 305 (IR), 341 (R), and 349 (IR) cm^{-1}) and for Pt_2(dba)$_3$ (314 (R), 325 (IR), 349 (IR), 393 (IR) cm^{-1}) and with those for the $M(C_2H_4)_3$ complexes (M = Ni, Pd, Pt).[10d] (b) The FT-IR spectra were recorded on a D002 BOMEM instrument with a resolution of 4 cm^{-1} and the use of 200 scans. (c) The Raman spectra were obtained with a Nicolet FT-Raman spectrophotometer using a Nd:YAG laser (30-mW laser power), 400 scans, and 4-cm^{-1} resolution. (d) Csaszar, P.; Goggin, P. L.; Mink, J.; Spencer, J. L. *J. Organomet. Chem.* **1989**, *379*, 337.

(11) (a) The τ_e measurements were performed on a Photon Technology Int. LS-100 model instrument. Typically λ_{exc} = 520 nm, λ_{emi} = 750 nm. (b) The τ_e value for Pd_2(dba)$_3$ (8.3 μs) agrees with the values reported in the literature.[6,7,11c] (c) Harvey, P. D.; Gray, H. B. *Polyhedron* **1990**, *9*, 1949.

(12) (a) The emission quantum yields were measured by using $[Pt_2(P_2O_5H_2)_4]((CH_3(CH_2)_3)_4N)_4$ as a standard, Φ_e = 0.50.[12b] (b) Harvey, P. D. Unpublished results. (c) The Φ_e value for $[Pt_2(P_2O_5H_2)_4]K_4$ in a 2/1 ethylene glycol/water solution is 0.43 at 77 K: Markert, J. T.; Clements, D. P.; Corson, M. R.; Nagle, J. K. *Chem. Phys. Lett.* **1983**, *97*, 1983.

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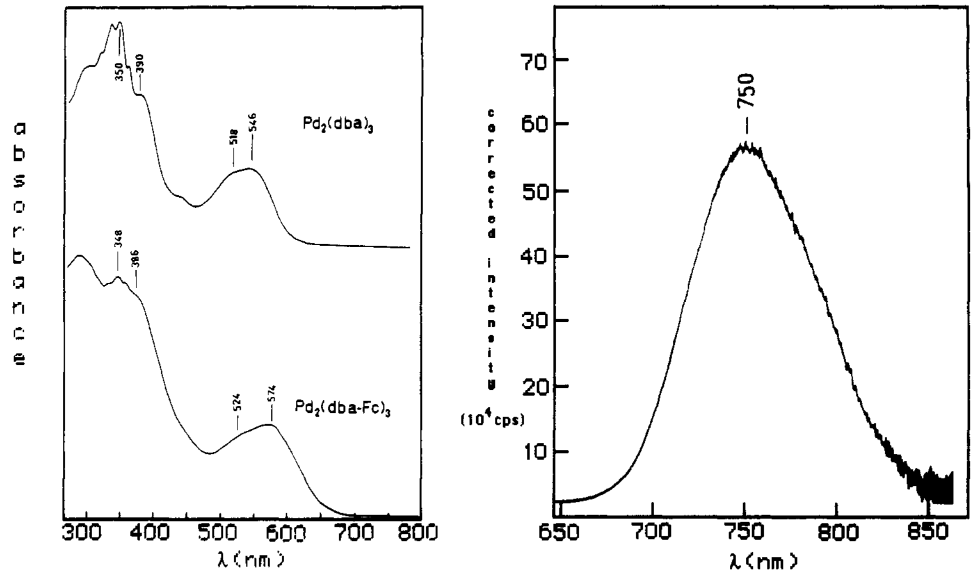

Figure 1. Left: Absorption spectra of $Pd_2(dba)_3$ and $Pd_2(dba\text{-}Fc)_3$ in 2-MeTHF at 77 K. Right: Emission spectra of $Pd_2(dba\text{-}Fc)_3$ in 2-MeTHF at 77 K.

Table I. Photophysical Parameters[a]

	$\nu_{max}^{(em)}/cm^{-1}$	$\tau_e/\mu s$[b]	Φ_e[c]	$k_r \times 10^{-4}/s^{-1}$	$k_{nr} \times 10^{-4}/s^{-1}$
$Pd_2(dba\text{-}Fc)_3$	13400	0.36 ± 0.02	0.0068 ± 0.0007	1.9	280
$Pd_2(dba)_3$	13500	8.3 ± 0.3	0.34 ± 0.03	4.1	8.0

[a] In 2-MeTHF glasses at 77 K. [b] λ_{exc} = 520 nm; λ_{emi} = 750 nm. [c] Quantum yield relative to $Pt_2(P_2O_5H_2)_4^{4-}$ (Φ_e = 0.50).

detectable luminescence in the complex indicates that the lowest energy triplet excited state is MLCT for $Pd_2(dba\text{-}Fc)_3$, not LF.[14]

Free dba-Fc in 0.1 M tetrabutylammonium hexafluorophosphate CH_2Cl_2 solutions exhibits two electrochemically reversible one-electron redox processes:[15] one ferrocenyl-localized oxidation (0.52 V vs SSCE) and one dba-localized reduction (−1.51 V vs SSCE). The $Pd_2(dba\text{-}Fc)_3$ cyclic voltammogram also exhibits an oxidation process at 0.50 V vs SSCE, but there is additionally an irreversible Pd_2-localized one-electron oxidation process at 1.21 V vs SSCE.[16] Upon bulk electrolysis (0.5 V vs SSCE) of both free dba-Fc and $Pd_2(dba\text{-}Fc)_3$, no color change occurs, but the visible spectra of the oxidized species exhibit a weak feature located at ~12 650 cm^{-1} (Figure 2) with absorptivities of 50 and ~150 M^{-1} cm^{-1}, respectively, which may be attributed to dba-Fc^+ and $Pd_2(dba\text{-}Fc)_3^{3+}$; these electronic bands thus indicate the presence of ferrocenium groups.[17] Bulk electrolysis of $Pd_2(dba\text{-}Fc)_3$ at 1.2 V vs SSCE at 298 K results in rapid decomposition of the material[18] with clear isosbestic points observed at 250, 280, and 365 nm. The presence of free dba-Fc in solution was detected by ^1H NMR spectroscopy during this electrolysis.

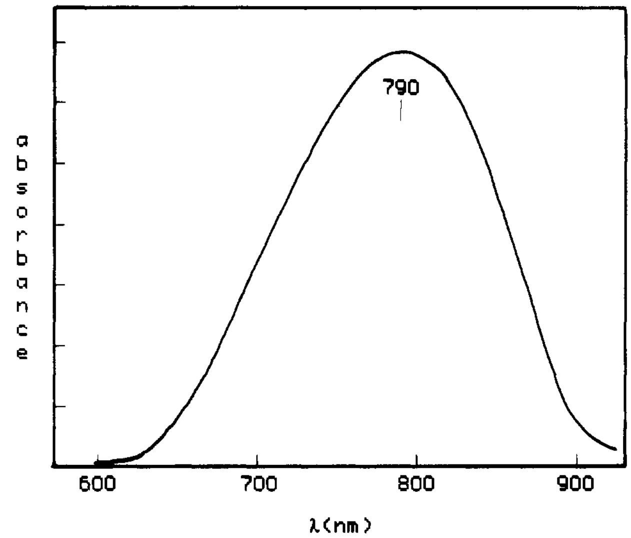

Figure 2. Absorption spectrum (600–900-nm range) of dba-Fc^+ in THF solution at 298 K.

In conclusion, the lowest energy excited states for $Pd_2(dba\text{-}Fc)_3$ and $Pd_2(dba\text{-}Fc)_3^{3+}$ are MLCT and LF (ferrocenium-localized), respectively. Thus, the results of this work demonstrate that one may electrochemically tune the nature of the excited states in the $M_2(dba)_3$ complexes by simple chemical modification with appropriate pendant groups. Considering the known photoinduced electron-accepting ability of the ferrocenium cationic group[17] and the potentially good electron donor properties of the electron-rich Pd(0) centers, it appears possible to tune photoinduced elec-

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(13) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979.

(14) (a) Ferrocene and its substituted derivatives are not luminescent in 77 K glasses.[13] (b) The LF and MLCT states appear to be close in energy and some mixing between these two states is possible. The fact that k_{nr} is 35-fold higher in $Pd_2(dba\text{-}Fc)_3$ as compared to $Pd_2(dba)_3$ supports this assumption.

(15) Experimental procedures for the cyclic voltammetric, coulometric, and spectroelectrochemical measurements have been reported elsewhere: Harvey, P. D.; Sharma, J. G. *Can. J. Chem.* **1990**, *68*, 223.

(16) (a) The M_2-localized oxidation processes have previously been reported for the $M_2(dba)_3$ complexes.[16b] (b) Ito, N.; Saji, T.; Aoyagui, S. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *144*, 153. (c) $Pd_2(dba\text{-}Fc)_3$ in solution at 298 K slowly decomposes to form free dba-Fc and Pd(0). Best results were obtained when the experiments were performed at low temperature (−45 °C). Nonetheless, the coulometric results are approximate values with an experimental error of ±15%.

(17) The lowest energy absorption LF band for the ferrocenium cation is located at 16 100 cm^{-1}.[4] The red shift in ν_{max} on going from ferrocenium to dba-Fc^+ is attributed to a normal substitution effect, and the same band assignment is made for oxidized dba-Fc and oxidized $Pd_2(dba\text{-}Fc)_3$. There has been no attempt to isolate these species.

(18) Electrolysis was completed within 10 min; therefore, the observed decomposition was not due to $Pd_2(dba\text{-}Fc)_3$, which decomposes slowly in solution.

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tron-transfer reactivity in these systems. Picosecond flash photolysis studies on $M_2(dba)_3$ (M = Pd, Pt) and $Pd_2(dba\text{-}Fc)_3$ are in progress.

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(20) To whom correspondence should be addressed.

(21) Present address: Department of Chemistry, Beijing University, Beijing, China.

Dēpartement de chimie
Universitē de Sherbrooke
Sherbrooke, PQ, J1K 2R1 Canada

Pierre D. Harvey*,[20]
Liangbing Gan[21]

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Reactions of Molybdenum(0) Tricarbonyl Complexes with 8-Azidoquinoline. Crystal Structure of the Phosphinimine Complex $Mo(CO)_4[N(PPh_3)(C_9H_6N)]$ and Evidence for a Bent Nitrene

The vast majority of monomeric, transition-metal nitrene (or imido) complexes that have been spectroscopically or structurally characterized are composed of high oxidation state metals with linear M–N–R units and triple bonds between M and N.[1] With the exception of several recent examples, the nitrene ligands in these complexes are very unreactive.[2] The bent M–N–R form, a geometry that is more rare, is predicted for low oxidation state metal complexes and/or when the formation of a triple bond between metal and nitrogen would violate the 18-electron rule.[3] Substantial bending of the M–N–R unit implies sp^2 hybridization at N, a M–N double bond, and a more nucleophilic nitrogen. Low-valent metal nitrene complexes have been proposed as transient intermediates in a variety of stoichiometric and catalytic reactions involving N–C or N–O bond cleavage and formation.[4] However, only recently has a tungsten(0) nitrene complex been trapped with triphenylphosphine to form the phosphinimine complex $(CO)_5W[N(PPh_3)Ph]$.[5]

Inspired by the work of Sloan and Thornton on high-valent metal nitrene complexes, we hypothesized that a low-valent transition-metal bent nitrene complex may be stabilized through incorporation of the nitrene into a chelate ring.[6] We chose 8-azidoquinoline because (1) formation of a nitrene ligand from the reaction of an organic azide with a metal complex is a common synthetic route for high oxidation state nitrene complexes[7] and (2) coordination of this ligand would produce a five-membered chelate ring incorporating a bent M═N—R unit. Herein we report the reactions of 8-azidoquinoline with *fac*-$Mo(CO)_3(CH_3CN)_2(L)$ [L = PPh_3 (**1a**), CH_3CN (**1b**), $P(OMe_3)_3$ (**1c**), $P(OEt_3)_3$ (**1d**)]. The crystal structure of $Mo(CO)_4[N(PPh_3)(C_9H_6N)]\cdot CH_3CN$ (**2**), containing a coordinated phosphinimine ligand, has been determined. A molybdenum(0)–bent nitrene appears to play a key role in the formation of the phosphinimine complex.

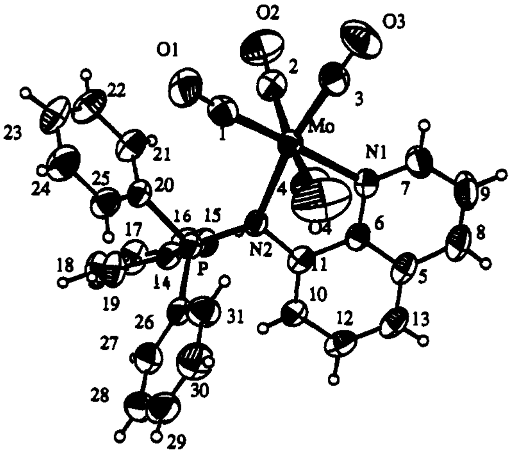

Figure 1. ORTEP drawing[16c] of $Mo(CO)_4(C_9H_6N_2)P(C_6H_5)_3\cdot CH_3CN$ (CH_3CN molecule omitted from the drawing). Thermal ellipsoids for non-hydrogen atoms are drawn at the 50% probability level; for hydrogen atoms the sphere radius is divided by 10. Carbon atoms are labeled by a single number (the same is used for the associated H atom, represented by a small circle). Selected bond lengths (Å): Mo–N(1), 2.245 (2); Mo–N(2), 2.312 (2); N(2)–P, 1.626 (2). Selected bond angles (deg): Mo–N(2)–P, 127.4 (1); Mo–N(2)–C(11), 113.9 (2); C(11)–N(2)–P, 117.9 (2).

Addition of **1a** in acetonitrile solution to 1 equiv of crystalline 8-azidoquinoline at −5 °C produces a dark red-brown solution within minutes.[8,9] After the solution was stirred at −5 °C for 1 h, the solution IR spectrum, at room temperature, reveals that the tricarbonyl pattern for **1a** (1925, 1818, 1799 cm^{-1}) has been replaced by a complex pattern of overlapping bands. The appearance of a band in the region just above 2000 cm^{-1} is suggestive of the formation of a cis-substituted tetracarbonyl species.[11] Also, the strong azide band, $\nu(N_3)$ at 2118 cm^{-1}, has completely dis-

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(2) Recent examples of reactive nitrene complexes include $Cp_2Zr(NR)$,[2a] $Cp^*Ir(NR)$,[2b] and $[Tp'(CO)_2W(NR)]^+$ [Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate].[2c] (a) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729. (b) Glueck, D. S.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2721. (c) Luan, L.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 8190.

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(7) Cenini, S.; La Monica, G. *Inorg. Chim. Acta* **1976**, *18*, 279. See also refs 1 and 3.

(8) 8-Azidoquinoline[8a] and **1a**[8b–d] are prepared according to published procedures. (a) The synthesis of aryl azides as reported by Smith and Brown (general procedure A) is used to prepare 8-azidoquinoline as pale yellow needles in 89% yield. Anal. Calcd (found) for $C_9H_6N_4$: C, 63.52 (63.56); H, 3.55 (3.46); N, 32.92 (32.55). Smith, P. A. S.; Brown, B. B. *J. Am. Chem. Soc.* **1951**, *73*, 2438. (b) Ross, B. L.; Grasselli, J. G.; Ritchey, W. M.; Kaesz, H. D. *Inorg. Chem.* **1963**, *2*, 1023. (c) Dobson, G. R.; Amr El Sayed, M. F.; Stolz, I. W.; Sheline, R. K. *Inorg. Chem.* **1962**, *1*, 526. (d) Tate, D. P.; Knipple, W. R.; Augl, I. M. *Inorg. Chem.* **1962**, *1*, 433.

(9) All reactions (excluding the preparation of 8-azidoquinoline) are done under N_2 by using standard Schlenk techniques.[10] Acetonitrile is dried in an inert atmosphere by refluxing over CaH_2. Photolysis experiments are carried out with Pyrex-filtered light from an Oriel 350-W high-pressure Hg arc lamp. Complex **1a** is prepared in situ by addition of 1 equiv of PPh_3 (129 mg, 0.5 mmol) to an CH_3CN solution of **1b** (generated by photolysis of 0.5 mmol of $Mo(CO)_6$ in 25–30 mL of CH_3CN). The solution of **1a** is cooled in an ice/salt bath (−5 °C) and added to 84 mg (0.5 mmol) of solid 8-azidoquinoline, also at −5 °C. Reactions are monitored in the IR region (at room temperature) by following the disappearance of the azide band [ν(N═N═N)] at 2118 cm^{-1}, as well as changes in the metal carbonyl bands.

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