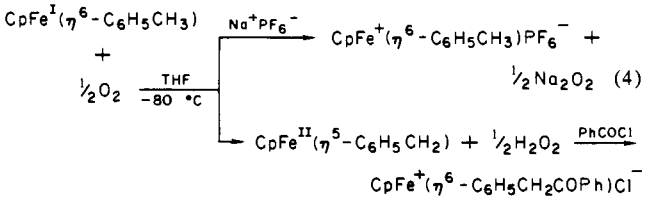
Table II. Salt Effect on the Reactivity of $O_2^{-}\cdot$ as a Nucleophile in the Reaction $3 \xrightarrow[-80\ °C,\ THF]{O_2} 4$ (2)[a]

M^+X^- [b]	4	$3^+PF_6^-$
without	100	0
$K^+PF_6^-$ + 18-6 (stoich)	60	40
$K^+PF_6^-$	30	70
$Na^+PF_6^-$	0	100

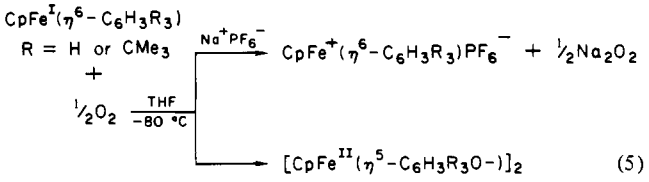
[a] See also eq 5 and 6. Percent of 4 and $3^+PF_6^-$ determined by weight (reactions are immediate). [b] Concentrations of both 3 and the salt in THF (30 mL) are 0.067 mol L^{-1}; $Na^+PF_6^-$ produces the same salt effect in DME.

dark-red C–H activation products are thermally unstable above −50 °C but reaction with PhCOCl at −80 °C (3 h) gives the benzoylation product even in the case of the most unstable parent complex $CpFe^{II}(\eta^5\text{-}C_6H_5{=}CH_2)$ (eq 4). In this later case, a

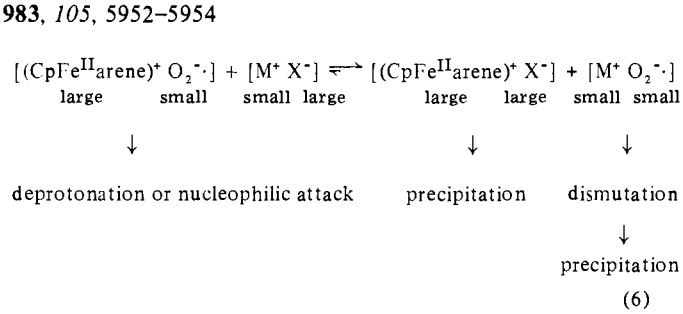


$\{^1H\}^{13}C$ NMR spectrum recorded at −80 °C subsequent to reaction between $^1/_2$ mol of O_2 and $CpFe^I(C_6H_5CH_3)$ in toluene-d_8 at −80 °C and filtration reveals the presence of the uncoordinated cyclohexadienyl carbon (δ 135 vs. Me_4Si).[10]

Orange dimeric peroxides[6,11] are characterized in the cases of the reactions of $CpFe^I(C_6H_6)$ and $CpFe^I(1,3,5\text{-}t\text{-}Bu_3C_6H_3)$ and $^1/_2$ mol of O_2 in the absence of $NaPF_6$ (−80 °C, fast) (eq 5). Thus



it turns out that a stoichiometric amount of $NaPF_6$ in THF solution changes the course of the reactions in the case of benzylic C–H activation as well as in the case of the formation of dimeric neutral peroxides. If only $^1/_2$ mol of $NaPF_6$ is added to a THF solution of **1**, addition of $^1/_2$ mol of O_2 at −80 °C leads to the formation of $^1/_2$ mol of **2** and $^1/_2$ mol of $\mathbf{1}^+\ PF_6^- + {}^1/_4$ mol of Na_2O_2. This salt effect[12] is confirmed by using other salts such as KPF_6, $n\text{-}Bu_4NPF_6$, $NaBF_4$, and NaF (Table I) in the reaction of O_2 with **1**. Whereas the salt effect is "quantitative" with $NaPF_6$, it decreases as the size of the cation increases and as the size of the anion decreases. Similar observations were obtained in the formation of **4** from **3** (Table II). Along this line, the salt effects on both reactions are inhibited by the presence of the suitable crown ether (18–6 with K^+). Note that since 18-crown-6 is required in reactions of KO_2 in THF, salt effects could not be observed before this strategy to generate $O_2^{-}\cdot$ was developed. These data are obviously in agreement with $O_2^{-}\cdot$ as intermediate in both the C–H activation and the formation of dimeric peroxide. This conclusion is also supported by the characteristic EPR spectra



of $O_2^{-}\cdot$ in frozen THF solution in the presence or absence of $NaPF_6$ and/or of benzylic hydrogen(s).[13]

The present observations indicate that ion exchange due to their relative sizes occurs in the ion pairs as shown in eq 6, this process being faster than reaction of $O_2^{-}\cdot$ in the cage.

Additional driving forces shifting this equilibrium to the right are (i) the alkali-cation-induced disproportionation of superoxide to peroxide[14] and (ii) the precipitation of both Na_2O_2 and the organometallic PF_6 salt. However the competition between the interaction of the alkali cation with its counteranion and with $O_2^{-}\cdot$ is the major factor in view of the considerable variation of salt effects obtained upon changing either the alkali cation or its counteranion (Tables I and II).

Acknowledgment. We are grateful to Dr. Bianca Tchoubar for invaluable discussions and to the CNRS for financial support (ATP No. 9812).

Registry No. 1, 70414-92-5; **2**, 70414-93-6; **3**, 51812-05-6; **4**, 83617-47-4; O_2, 7782-44-7; $O_2^{-}\cdot$, 11062-77-4; $n\text{-}Bu_4N^+PF_6^-$, 109-63-5; $K^+PF_6^-$, 17084-13-8; 18-crown-6, 17455-13-9; $Na^+PF_6^-$, 21324-39-0; $Na^+BF_4^-$, 13755-29-8; Na^+F^-, 7681-49-4; $CpFe^I$(toluene), 69022-30-6; $CpFe^I$(mesitylene), 51812-08-9; $CpFe^I$(pentamethylbenzene), 76747-94-9; $CpFe^I$(ethylbenzene), 78230-46-3; $CpFe^I$(fluorene), 69022-32-8; $CpFe^+(\eta^6\text{-}C_6H_5CH_2COPh)PF_6^-$, 86584-12-5; $[CpFe(\eta^5\text{-}C_6H_3(t\text{-}Bu)_3O)]_2$, 86584-13-6; $CpFe^I(\eta^6\text{-}C_6H_3(t\text{-}Bu)_3)$, 83528-72-7.

(10) ^{13}C NMR data for $CpFe^{II}(\eta^5\text{-}C_6H_5{=}CH_2)$ ($C_6D_5CD_3$, −80 °C) 134.8 (C uncoordinated), 91.4 (*p*-C), 80.6 (*m*-C), 52.5 (*o*-C), 72.5 (Cp), 73.2 (CH_2). $CpFe^+(\eta^6\text{-}C_6H_5CH_2COPh)PF_6^-$ ^1H NMR (CD_3COCD_3) 7.70 (m, Ph, 5 H), 6.50 (s, C_6H_5, 5 H), 5.26 (s, Cp, 5 H), 4.86 (s, CH_2, 2 H); ^{13}C NMR (CD_3CN) 196.7 (CO), 137.3, 135.2, 131.0, 129.8 (Ph), 101.6 (C quaternary C_6H_5), 91.2, 90.5, 90.0 (*p*-, *m*-, *o*-, C_6H_5), 41.7 (CH_2), 78.8 (Cp).

(11) $[CpFe(\eta^5\text{-}C_6H_6O\text{–})]_2$ ^{13}C NMR (C_6D_6) 72.8 (Cp), 79.8 (*p*-C), 77.9 (*m*-C), 73.3 (sp^3C), 37.1 (*o*-C). $[CpFe(\eta^5\text{-}C_6H_3Bu_3{}^tO\text{–})]_2$ ^1H NMR (C_6D_6) 4.10 (s, Cp, 5 H), 5.43 (s, *m*-H, 2 H), 3.92 (s, CHO, 1 H), 1.55 (s, CH_3, 18 H), 1.50 (s, CH_3, 9 H); ^{13}C NMR (C_6D_6, 15 °C) 74.9 (Cp), 88.0 (*p*-C), 77.9 (*m*-C), 53.9 (*o*-C), 37.9 ($p\text{-}C(CH_3)_3$), 37.6 ($o\text{-}C(CH_3)_3$), 74.7 (sp^3C), 37.9, 37.6 ($C(CH_3)_3$).

(12) For useful discussions of salt effects, see: Gordon, J. E. "The Organic Chemistry of Electrolyte Solutions"; Wiley: New York, 1975.

(13) O_2 was allowed to diffuse slowly into EPR tubes containing frozen THF or DME solutions of the $CpFe^I$ (arene) complexes at 173–180 K (arene = C_6H_6, $C_6H_5CH_3$, $C_6(CH_3)_6$) in the presence or absence of $Na^+PF_6^-$. In all these cases, the spectrum of $O_2^{-}\cdot$ was obtained (77 K, $g_{\parallel} = 2.091$, $g_{\perp} = 2.005$). See also ref 3b and 5c.

(14) It is known that disproportionation of superoxide radical anion to peroxide is catalyzed by protons or transition-metal ions, as, for instance, in superoxide dismutase (SOD).[2c,3] We are not aware of precedents indicating that alkali cations can also effect this process, but we propose that this is so in our system. Alternatively, $O_2^{-}\cdot$ could be reduced by the Fe^I complex, a thermodynamically unfavored process that would require an overpotential of ca. 0.6 V.

Multiple-State Emission and Intramolecular Electron-Transfer Quenching in Rhenium(I) Bipyridine Based Chromophore–Quencher Complexes

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Electron-transfer processes involving excited-state quenching in which "electron–electron hole separation" is achieved are an important initial step in many redox photosensitization schemes[1]

(1) (a) Meyer, T. J. *Acc. Chem. Res.* **1978**, *11*, 94. (b) Whitten, D. G. *Ibid.* **1980**, *13*, 83. (c) Meyer, T. J. *Prog. Inorg. Chem.* **1983**, *30*, 389–440. (d) Balzani, V.; Bolleta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1. (e) Sutin, N.; Creutz, C. *Pure Appl. Chem.* **1980**, *52*, 2717. (f) Sutin, N. *J. Photochem.* **1979**, *10*, 19. (g) Kalyanasundaran, K. *Coord. Chem. Rev.* **1982**, *46*, 159.

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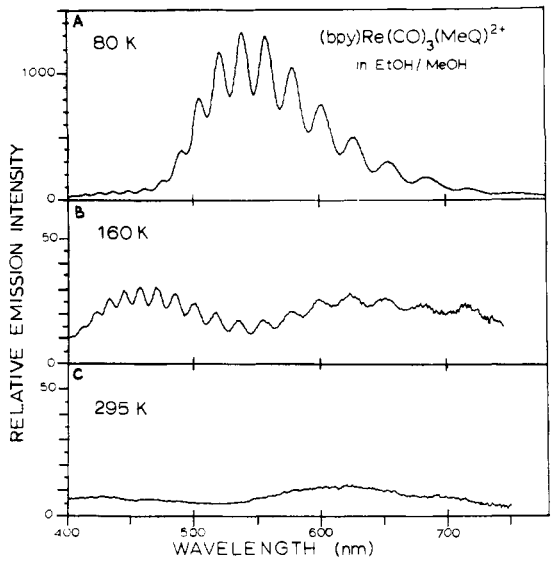

Figure 1. Corrected emission spectra for $[(bpy)Re(CO)_3(MeQ)]^{2+}$ as the PF_6^- salt in 4:1 ethanol/methanol, bubble degassed with dry N_2. Notice the difference in vertical scales between the 80 K and the 160 and 295 K spectra. Concentration of complex is ~1 mM. λ_{ex} = 380 nm. Note ref 8a. (A) At 80 K, (B) at 160 K, (C) at 295 K.

(eq 1). Related but intramolecular phenomena have been ob-

$$Ru(bpy)_3^{2+*} + PQ^{2+} \rightarrow Ru(bpy)_3^{3+} + PQ^+ \quad (1)$$

(bpy is 2,2′-bipyridine;

PQ^{2+} is *N,N′*-dimethyl-4,4′-bipyridine)

served in complexes where the redox quenchers are chemically linked to the chromophore,[2,3] e.g., $[(bpy)_2Ru^{II}(MeQ^+)_2]^{4+}$. Such chromophore–quencher complexes are attractive candidates for the development of chemical systems that display directed charge-transfer characteristics or in which intramolecular sensitization occurs at a second, possibly catalytic site.[4]

From the synthetic point of view an attractive system for such studies is based on complexes of the type $[(bpy)(CO)_3Re^IL]^+$ where the background synthetic chemistry and the properties of the $\pi^*(bpy) \leftarrow d\pi(Re^I)$ (MLCT) charge-transfer excited states have been investigated, most notably by Wrighton and co-workers.[5] We have used procedures developed in their work to prepare the new intramolecular "chromophore–quencher" complexes $[(bpy)Re^I(CO)_3L]^{2+}$ (L = *N*-methyl-4,4′-bipyridine (MeQ^+), *N*-benzyl-4,4′-bipyridine (BzQ^+)) and report here in a preliminary fashion on the existence of three remarkable photophysical properties: (1) the appearance of a well-defined, low-energy vibrational progression in emission spectra, (2) the appearance of a short-lived emission attributed to MLCT "fluorescence", and (3) the existence of an intramolecular electron-transfer quenching that is "triggered" by the change in solvent orientational mobility associated with the glass → fluid transition.

Cyclic voltammograms of the complexes as PF_6^- salts in 0.1 M $[NEt_4]ClO_4$/acetonitrile solution show the expected largely irreversible $Re^{II/I}$ couple[5] at E_{peak}^{ox} = +1.85 V vs. the saturated sodium chloride calomel electrode (SSCE). Reversible reductions are observed at $E_{1/2}$ = −0.71 V and −0.68 V for L = MeQ^+ and BzQ^+, respectively, which are centered on the pyridinium ligand. They are followed by bpy-based reduction waves at −1.13 V and −1.18 V, respectively. UV–vis absorption spectra in acetonitrile solution are dominated by the usual metal-to-ligand charge-transfer (MLCT) bands ($\pi^*(bpy) \leftarrow d\pi(Re^I)$)[5] at 339 nm for L = MeQ^+ and at 342 nm for BzQ^+. Ligand localized transitions also occur but at higher energies as reported by Wrighton and co-workers.[6]

The existence of the three unusual features mentioned above are illustrated by the emission spectra for the complex $[(bpy)Re(CO)_3MeQ]^{2+}$ in 4:1 ethanol/methanol shown in Figure 1. At 80 K emission from $[(bpy)Re(CO)_3MeQ]^{2+}$ and related $Re^I(bpy)$ complexes is dominated by radiative decay from a bpy-based, largely "triplet" metal-to-ligand charge-transfer (MLCT) excited state or states,[7] $(bpy^-\cdot)Re^{II}(CO)_3L^+ \rightarrow (bpy)Re^I(CO)_3L^+$.

From the figure a striking feature in the first two spectra is the appearance of the well-resolved and extensive vibrational structure with average vibrational spacings of ~630 cm^{-1}.[8a] Similar progressions exist for a series of complexes of the type $[(bpy)Re(CO)_3L]^+$ (L = PPh_3, 4-ethylpyridine, 4,4′-bpy) and $[(bpy)_2Os(CO)L]^{2+}$,[8b] and their origins may lie in a δ(M–C–O) bending vibration[9] of the Re–CO groups. Somewhat related progressions have been observed in MLCT absorption[10] and UPS spectra[11] of other carbonyl-containing compounds and by Tutt et al. in the low-temperature emission spectrum of $W(CO)_5py$ (py is pyridine).[12]

For the complexes $[(bpy)Re(CO)_3L]^{2+}$, L = MeQ^+ and BzQ^+, a dramatic decrease in lifetime (for L = BzQ^+ 4841 ± 41 ns at 80 K to <20 ns at 150 K) and emission intensity for the bpy-based MLCT state is observed at temperatures above the glass → fluid transition (>130 K).[13] For $[(bpy)Re(CO)_3BzQ]^{2+}$ the loss of emission from the ^{3}MLCT state (λ_{max} = 508 nm) is paralleled by the appearance of a weak, red-shifted (λ_{max} = 620 nm) emission that has a nearly temperature independent lifetime of ~1715 ± 369 ns in the fluid from 130 to 220 K. For $[(bpy)Re(CO)_3(MeQ)]^{2+}$ excited-state distortions in the ^{3}MLCT state are apparently greater and, as shown in part C of the figure, the ^{3}MLCT and ~620-nm emissions overlap. The appearance of the weak, red-shifted emission is indicative of an intramolecular, electron-transfer quenching process followed by emission from the lower, BzQ^+-based MLCT state, $[(bpy^-\cdot)Re^{II}(CO)_3(BzQ)]^{2+} \rightarrow [(bpy)Re^{II}(CO)_3(BzQ^-\cdot)]^{2+} \xrightarrow{-h\nu} [(bpy)Re^I(CO)_3(BzQ)]^{2+}$.[2]

The ^{3}MLCT(bpy) → ^{3}MLCT(BzQ) transition appears to be triggered by the enhanced orientational mobility associated with the glass → fluid transition. In a Lexan (polycarbonate resin) film at room temperature the strong ^{3}MLCT(bpy) luminescence is unquenched. In addition, in the film the emission maximum at ~520 nm is constant from 80 to 290 K, and the lifetime at room temperature (1538 ± 8 ns) is comparable to the lifetime in the EtOH/MeOH glass. An important component of the glass

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(7) Note that the terms "triplet" and "singlet" are only useful in a relative sense. Spin–orbit coupling gives rise to considerable mixing of the "pure" singlet and triplet states in related complexes of osmium. See: Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 3967. Kober, E. M. Ph.D. Thesis, University of North Carolina, 1982.

(8) (a) In order to observe the vibrational structure the solvents must be rigorously dried (distilled from the corresponding magnesium alkoxide). Structured emissions have also been observed in 2-MeTHF glasses, frozen methylene chloride solutions, and a Lexan film at room temperature. (b) Westmoreland, T. D.; Le Bozec, H., unpublished results.

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(13) $[(bpy)Re(CO)_3(4\text{-}Et(py))]^+$ shows a less dramatic decrease in lifetime (4440 ± 9 ns at 80 K to 244 ± 1 ns at 180 K) and a shift to a lower emission energy as the solvent melts. This decrease in lifetime with emission energy is quantitatively consistent with the energy-gap law for radiationless decay (ref 5c: Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630).

→ fluid triggering effect is, no doubt, the necessity of the two aromatic rings of the quencher ligand to assume a coplanar arrangement before quenching can occur. In the methyl substituted complex $[(bpy)_2Os(CO)N,3,3'\text{-trimethyl-}4,4'\text{-bipyridine}]^{3+}$, flattening can not occur because of steric repulsion; electrochemical measurements show that the pyridinium-based reduction is at −1.06 V vs. SSCE, and intramolecular quenching of the ^{3}MLCT(bpy) state in fluid solution is not observed.[8b] The analogous Re complex is currently under investigation.

The third novel feature in the figure is the appearance of clear evidence for a broad, higher energy luminescence at 400–525 nm. It seems clear that the higher energy emission must occur from a "singlet" analogue of the ^{3}MLCT(bpy) state on the basis of the following evidence: vibrational progressions for both high- and low-energy emissions are nearly the same within experimental error and lifetime studies show that even at 80 K the lifetime of the higher energy emission is <20 ns.

It has been suggested that a ^{1}MLCT(bpy)-based emission does occur following excitation of $Ru(bpy)_3^{2+}$ on the basis of the results of lifetime studies,[14] but the emission spectra shown here provide direct spectral evidence for such an emission for this type of chromophore. Our ability to observe the fluorescence so clearly in cold fluid solution is a direct consequence of intramolecular quenching of the relatively long-lived ^{3}MLCT(bpy) state by bound BzQ^+ or MeQ^+. At 80 K we estimate that $\Phi_{em}(^1MLCT)/\Phi_{em}(^3MLCT) \simeq 0.02$. By 160 K, the intensities of the two emissions are comparable as shown in part B of the figure. It appears that at low temperature where intramolecular quenching by BzQ^+ or MeQ^+ is unimportant, the absolute radiative efficiency from the ^{1}MLCT(bpy) state is low, suggesting that "fluorescence" competes unfavorably with "intersystem crossing", ^{1}MLCT(bpy) → ^{3}MLCT(bpy), which is known to be the case for $Ru(bpy)_3^{2+}$ at room temperature.[15]

Acknowledgments are made to the National Science Foundation under Grants CHE-8008922 and CHE-7920114 and to NATO and CNRS France for support of H.L'B.

Registry No. $[(bpy)Re(CO)_3(MeQ)]^{2+}$, 86695-84-3; $[(bpy)Re(CO)_3(BzQ)]^{2+}$, 86695-85-4.

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Alkyl, Hydride, and Dinitrogen 1,2-Bis(dimethylphosphino)ethane Complexes of Chromium. Crystal Structures of $Cr(CH_3)_2(dmpe)_2$, $CrH_4(dmpe)_2$, and $Cr(N_2)_2(dmpe)_2$

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Inorganic and organometallic complexes of first row transition metals are more labile than their second and third row analogues,[1] and consequently they should exhibit relatively enhanced reactivity. Often, however, second and third row metal compounds have no first row counterparts, and in many instances this may be attributed to the increased labilities of the latter, which make decomposition pathways more accessible. In particular, apart from some carbonyl species, phosphine derivatives of the early first row metals are rare.[2] We now report some chromium complexes of the chelating phosphine ligand 1,2-bis(dimethylphosphino)ethane (dmpe), notably the first example of a mononuclear Cr^{II} alkyl, a Cr^{IV} hydride, and the first stable Cr^0 dinitrogen complex to be fully structurally characterized, unlike previous examples that have been observed in solution.[3]

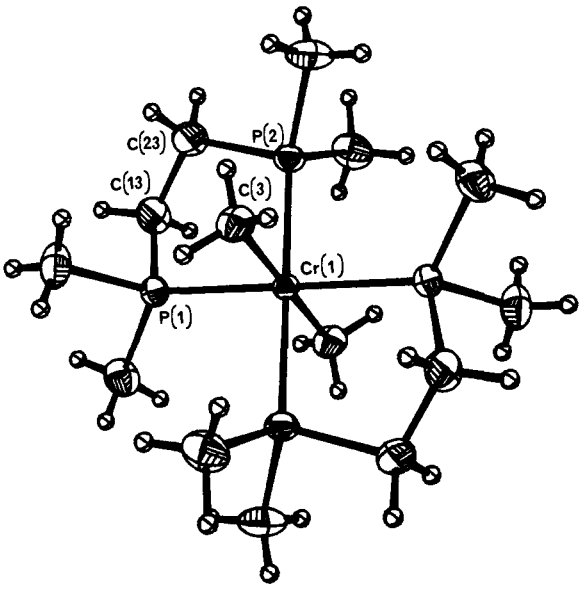

Figure 1. Structure of $CrMe_2(dmpe)_2$. Important bond lengths (Å) and angles (deg): Cr(1)–C(3), 2.168 (4); Cr(1)–P(1), 2.342 (1); Cr(1)–P(2), 2.349 (1); Cr(1)–C(3)–H(31), 121 (2); Cr(1)–C(3)–H(32), 108 (3); Cr(1)–C(3)–H(33), 108 (2); P(2)–Cr(1)–P(1), 82.7 (1); C(3)–Cr(1)–P(1), 87.2 (2); C(3)–Cr(1)–P(2), 89.6 (2).

Evidence for the formation of adducts of divalent chromium halides with phosphine ligands is tenuous.[2,4] However, the interaction of $CrCl_2(thf)$[5] with 2 equiv of dmpe in toluene rapidly yields a bright yellow-green solution, from which large prisms of $CrCl_2(dmpe)_2$[6] may be isolated. This complex is paramagnetic with a magnetic moment of 2.76 μ_B in solution at room temperature, indicating a low-spin d^4 configuration.

The only two neutral Cr^{II} alkyls known are diamagnetic, quadruply bonded dimers.[7] By contrast, the alkylation of $CrCl_2(dmpe)_2$ with methyllithium in diethyl ether gives mononuclear, red-orange $CrMe_2(dmpe)_2$[8] in high yield. This complex is also low spin (μ = 2.7 μ_B). The infrared spectrum exhibits a rather low C–H stretching frequency of 2780 cm^{-1}, which can be assigned to the CrMe groups. It is likely that the lowering of these vibrations is associated with the electronic unsaturation (16e) of the metal center.

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(6) Anal. Calcd: C, 34.1; H, 7.66; Cl, 16.7; P, 29.3; Cr, 12.3. Found: C, 34.1; H, 7.55; Cl, 16.4; P, 29.2; Cr, 12.1. Mp 270 °C dec; ^{1}H NMR (PhH-d_6, 25 °C) δ −13.1 (PCH_2, s, $W_{1/2}$ = 240 Hz), −33.5 (PMe_2, s, $W_{1/2}$ = 310 Hz); MS, m/e 422 (M^+, 1.5%).
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(8) Anal. Calcd: C, 44.0; H, 10.02, P, 32.4; Cl, 0. Found: C, 44.0; H, 10.18; P, 32.9; Cl, <0.4. Mp 195 °C dec; ^{1}H NMR (PhH-d_6, 25 °C) δ 0.9 (PCH_2, s, $W_{1/2}$ = 260 Hz), −28.6 (PMe_2, s, $W_{1/2}$ = 310 Hz); MS, m/e 387 (M^+, 1.7%).

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