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)2]Y3,3′-trimethyl-1,4′-bipyridine)23, 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 3MLCT(bpy) state in fluid solution is not observed.25 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" analog of the 3MLCT(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 1MLCT(bpy)-based emission does occur following excitation of Ru(bpy)2+26 on the basis of the results of lifetime studies,27 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 3MLCT(bpy) state by bound BzQ+ or MeQ+. At 80 K we estimate that Φem(1MLCT)/Φem(3MLCT) ≈ 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 1MLCT(bpy) state is low, suggesting that "fluorescence" competes unfavorably with "intersystem crossing", 1MLCT(bpy) → 3MLCT(bpy), which is known to be the case for Ru(bpy)2+26 at room temperature.15

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


Alkyl, Hydride, and Dinitrogen
1,2-Bis(dimethylphosphino)ethane Complexes of Chromium. Crystal Structures of Cr(CH3)2(dmpe)2, CrH4(dmpe)2, and Cr(N3)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 at-

Inorganic and organometallic complexes of first row transition metals are more labile than their second and third row analogues, 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 at-

The X-ray structure of CrMe₂(dmpe)₂ is given in Figure 1, along with some of the geometric parameters. The Cr-P distances of ca. 2.25 Å are rather shorter than those of 2.460 Å in the dimer Cr₂(CH₃SiMe₃)₄(PMe₃)₂. The metal-bound methyl groups show no Cr--H interactions, such as those recently observed in TiMeCl(dmpe), despite the low electron count. The Cr-C-H angles of 108°, 108°, and 121° do show a small but statistically significant scatter. However, the distortion is probably not chemically significant; furthermore, it is not clear whether any distortion, if real, would be a reflection of electronic or steric effects.

Neutral hydrides of chromium are known only in the divalent oxidation state of chromium. The reaction of CrCl₂(dmpe)₂ with n-butyllithium in hexane under a hydrogen atmosphere gives a dark-orange solution from which yellow CrH₄(dmpe)₂ may be isolated. This complex is diamagnetic, and the hydride ligands are bound in a linear configuration, Cr-N-N being 177.3°. The N-N distance at 0.985 Å, which counteracts the usual decrease in metal radii as the oxidation state increases.

The X-ray crystal structure of CrH₄(dmpe)₂ is shown in Figure 2. The hydride, which has approximate interlocking trapezia are formed by P(1), P(3), H(1), H(2) and P(2), P(4), H(3), H(4), with the angle between the planes being about 108°.

Figure 2. Structure of CrH₄(dmpe)₂. Important bond lengths (Å) and angles (deg): Cr(1)--P(1), 2.258 (3); Cr(1)--P(2), 2.252 (3); Cr(1)--P(3), 2.258 (3); Cr(1)--P(4), 2.252 (3); Cr(1)--H(1), 1.60 (3); Cr(1)--H(2), 1.56 (3); Cr(1)--H(3), 1.53 (3); Cr(1)--H(4), 1.59 (3); P(2)--Cr(1)--P(1), 84.8 (1); P(3)--Cr(1)--P(4), 85.1 (1); P(3)--Cr(1)--P(1), 159.0 (1); P(2)--Cr(1)--P(2), 98.8 (1); P(4)--Cr(1)--P(1), 98.4 (1); H(1)--Cr(1)--H(2), 65 (2); H(3)--Cr(1)--H(4), 63 (2).

The proton-coupled 3¹P NMR spectrum is also a binomial quintet with the same composition detectable by NMR spectroscopy. All chromium dinitrogen complexes react with sodium amalgam in tetrahydrofuran under a dinitrogen atmosphere gives the diamagnetic trans-Cr(N₂)₂(dmpe)₂ as large red prisms in high yield. This product has a formal oxidation state of chromium.
of CrH2(dmpe)3 and Cr(N2)3(dmpe)3 have been known (for phosphines other than dmpe) for several years.19 We are currently investigating the reaction chemistry of these chromium species in relation to that of their heavier congeners.

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**Registry No.** CrCl2(dmpe), 86747-59-9; CrMe2(dmpe), 86784-82-9; CrH2(dmpe)3, 86747-56-0; Cr(N2)3(dmpe), 86765-89-1; CrCl3(THF), 36465-97-5; dmpe, 2936-60-9.

**Supplementary Material Available.** Synthesis of CrCl2(dmpe)3, CrMe2(dmpe)3, CrH2(dmpe)3, and Cr(N2)3(dmpe)3 and tables of atom coordinates, temperature factors, and bond lengths and angles for CrMe2(dmpe)3, CrH2(dmpe)3, and Cr(N2)3(dmpe)3 (9 pages). Ordering information is given on any current masthead page.

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18[(2,6)Pyridinon-6-yl] "Sextypyridine"

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For over five decades, sextypyridine I has been the synthetic target of numerous research groups. Although Chemical Abstracts affords no information concerning I, many diverse procedures have been alleged and/or suggested.2 The original and most obvious, albeit unsuccessful, route to I is via an Ullmann macrocyclization in which an appropriate dihalopyridine is heated in the presence of a metal surface. This procedure results in deleterious linear sites to wrap in an appropriate "metal template" to permit cyclization.3 To circumvent the necessity of this unfavored specific, rigid orientation prior to cyclization, we herein describe the first successful synthesis of the unsubstituted sextypyridine I (Scheme I) via an initial macrocyclization to give a flexible polyfunctional intermediate, from which the molecular rigidity is irreversibly introduced.

The SeO2 oxidation of 2, prepared by coupling of 2-bromo-6-picoline with Pd/C under phase-transfer conditions,4 gave di-aldehyde.5,6 Treatment of 3 with 1,3-propanediol and p-toluenesulfonic acid in refluxing toluene afforded the bis(dithiane) 4,8 as colorless needles. Lithiation of 4 in THF with n-BuLi at -45°C was followed by addition of 1,3-dibromopropane to give the tetrakis(dithiane) 5, which was not fully characterized but lacks the singlet at δ 5.43 in the 1H NMR. This macrocyclization proceeded best at -30 to -45°C over extended time (e.g., 3 days); shorter times and elevated temperatures gave rise to either side reactions or unchanged starting materials. Cleaveage of the protecting group of 5 with NBS in aqueous THF at 0°C by a known procedure6 gave 6.210 The convenient, one-step conversion of 1,5-diketones to a pyridine nucleus utilizes hydroxylamine13 under acidic conditions; thus, treatment of 6 with H2NOH in refluxing glacial acetic acid for 24 h generates sextypyridine I.122 The upfield shift (Δδ 0.5 ppm) of the 3.5-H in 1 vs. the central ring in anti-terpyridine further supports the syn configuration. This general methodology has been successfully applied14 to the construction of the remaining "pyridino" 18-crown-6 ethers2b.

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