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Communications

Pyrazolyl-Bridged Iridium Dimers. 14.[1] Steric Control in Ground-State Oxidative Addition of Methyl Iodide to Complexes Related to $[Ir(CO)_2(\mu\text{-pz})]_2$

It has long been recognized that steric influences can profoundly alter rates of reactions that occur at square transition-metal sites.[2] Thus, for example, nucleophilic replacement of Cl in $Pt(PEt_3)_2(R)Cl$ is 10^5 times slower for R = mesityl vs R = Ph, an effect attributed[3] to shielding by *o*-Me substituents of the Pt atom, and closely related arguments have since been invoked in the context of diplatinum chemistry by Puddephatt et al.[4] We were surprised, therefore, to read a recent analysis of the electronic structure of the diiridium(I) complexes[5,6] $[Ir(CO)_2(\mu\text{-L})]_2$ (**1**, L = pz, pzH = pyrazole; **2**, L = 3-Mepz; **3**, L = 3,5-Me_2pz) that in our view did not take proper account of such steric influences, while[7] at the same time inaccurately (citing ref 8) attributing to us the surmise that "shorter metal–metal distances generally lead to higher reactivity". We do not doubt that inductive release from pz Me substituents increases electron availability at the metal centers in **2** and **3** vs **1**, nor do we doubt that the calculated differences in $\sigma{:}\sigma^*$ orbital energy separation validly reflect this change. It is clear from the kinetic evidence presented below, however, that addition of MeI is in fact dramatically slower *in the ground state* to **2** and **3** vs **1**, i.e. in accord with our earlier qualitative suggestions.[8]

We have reported elsewhere[1] that addition of MeI to compound **1** occurs in two kinetically distinguishable steps, of which only the first (with $k_2 = 2.56 \times 10^{-2}$ M^{-1} s^{-1}, 293 K) is dependent on [MeI]. Analogous reactions of complexes **2**, **3**, and $[Ir(CO)_2(\mu\text{-}Me_3pz)]_2$ (**4**), the rates of which have been followed spectrophotometrically by using THF as solvent and under pseudo-first-order conditions, show first-order dependence on [MeI] and exhibit isosbestic points as is typified in Figure 1 for adduction of MeI with **3**. Second-order rate constants k_2 are compared in Table I. Analysis of the temperature dependence of k_2 determined activation free energies ΔG^*_{298} (by using Eyring plots to obtain ΔH^* and ΔS^*), values for which are also entered in Table I. It was further discovered that *these reactions* (*i.e.* of **2**–**4**) *are markedly accelerated by exposure to light*, in sharp contrast to the behavior of dimer **1**, which shows no such effect; thus, spectra recorded under normal laboratory lighting revealed isosbestics at slightly shifted wavelength (see Table I), with MeI addition occurring roughly 50 (to **3** or **4**) or 10 (**2**) times faster vs the k_2 values of Table I. Conversely, in the presence of either catechol or hydroquinone, the reaction of MeI with dimer **3** is slower by about an order of magnitude, and gives rise to an isosbestic at the wavelength (402 nm) characteristic of the dark reaction, while the latter is markedly accelerated by introduction of dibenzoyl peroxide, with absorbance changes fixing an isosbestic point at 395 nm (i.e. parallelling the light reaction, see Table I).

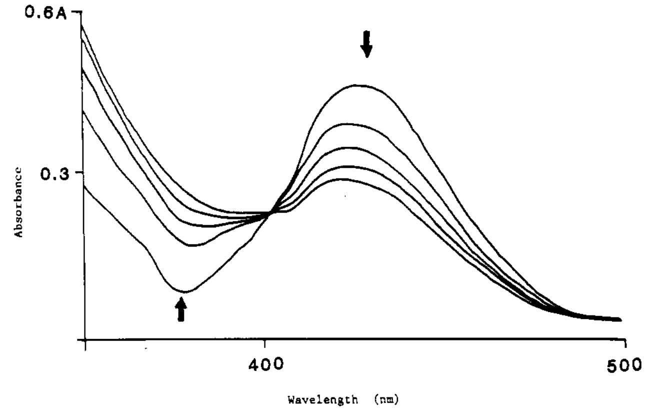

Figure 1. Spectral changes during reaction of MeI with dimer **3** in THF at 20 °C (scan intervals, 30 min). Initial concentrations: MeI, 200 μL/3 mL of THF (2 M); **3**, 0.19 mM.

Table I. Second-Order Rate Constants, k_2, and Free Energies of Activation, ΔG^*_{298}, for MeI Addition (THF Solution)

compd	k_2,[a] M^{-1} s^{-1}	ΔG^*_{298},[b] kJ mol^{-1}	N[c]	λ_i,[d] nm
$[Ir(CO)_2(\mu\text{-pz})]_2$ (**1**)	$2.56\ (6) \times 10^{-2}$	76 (1)	×1.2	393
$[Ir(CO)_2(\mu\text{-Mepz})]_2$ (**2**)	$2.3\ (3) \times 10^{-3}$	89 (3)	×12	395
$[Ir(CO)_2(\mu\text{-}Me_2pz)]_2$ (**3**)	$1.4\ (3) \times 10^{-4}$		×60	402
$[Ir(CO)_2(\mu\text{-}Me_3pz)]_2$ (**4**)	$1.5\ (2) \times 10^{-4}$	95 (2)	×53	410

[a] Rate constant for dark reaction, i.e. measured in a Perkin-Elmer Lambda 4B spectrophotometer cell compartment with exclusion of external light. [b] ΔH^* (kJ mol^{-1}), ΔS^* (J mol^{-1} K^{-1}), respectively, as follows: for **1**, 32 (2), −152 (8); for **2**, 26 (2), −211 (5); for **4**, 31 (1), −214 (3). [c] Approximate rate acceleration vs k_2 under laboratory lighting (see text). [d] Wavelength of isosbestic point determined by dark reaction data (e.g., see Figure 1); shifted to 395 nm for light reaction of **3** and 401 nm for light reaction of **4**.

It is clear from the manner in which the measured k_2 values (Table I) range over 2 orders of magnitude that addition at the d^8 metal centers in compounds **1**–**4** in reactions involving the electronic ground state of the binuclear configuration is controlled by steric effects[8] that restrict access to the axial coordination sites, although $[Ir(COD)(\mu\text{-pz})]_2$ (**5**) does react rather faster[1] than

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dimer **1** (Table I) as has been predicted[7] by electronic arguments. The existence of a parallel, light-promoted reaction manifold that is markedly susceptible to external radical influences but is relatively insensitive to steric effects suggests that an ET mechanism related to the excited-state behavior[9] of compound **5** may overtake the associatively activated thermal reaction[1] under appropriate conditions.

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Registry No. **1**, 96280-42-1; **2**, 117687-35-1; **3**, 82484-38-6; **4**, 123266-64-8; MeI, 74-88-4.

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Utility of the 2,6-Dimethylphenoxide Ligand in Providing Chloride- and Oxide-Free $[Y(OR)_3(\text{solvent})_a]_b$ Complexes with Accessible Coordination Sites

Recently, the alkoxide chemistry of yttrium, barium, and copper has been of interest, since hydrolysis of heteropolymetallic alkoxides of these metals via sol-gel processes[1,2] offers a route to high-purity superconducting oxides such as $YBa_2Cu_3O_{7-x}$.[3] Although alkoxide complexes of yttrium have been known for years,[4,5] the precise structure and composition of some of these compounds has only recently been verified by X-ray crystallography.[6-11] These studies have shown that, with simple ligands such as $OCMe_3$ and $OCHMe_2$, polymetallic complexes that incorporate halide and oxide ligands are formed instead of simple $Y(OR)_3$ species. To date, the only way to obtain a fully characterized homoleptic $Y(OR)_3$ complex has been to use the 2,6-di-*tert*-butylphenoxide ligand, a ligand so large that the unusually low coordination number of 3 is observed in $Y[OC_6H_3(t\text{-Bu})_2\text{-}2,6]_3$ (**1**).[11] We report here that the 2,6-dimethylphenoxide ligand[12,13] can provide halide- and oxide-free $[Y(OR)_3(\text{solvent})_a]_b$ complexes with enough steric flexibility to achieve five- and six-coordination and to form bridged bimetallic species.

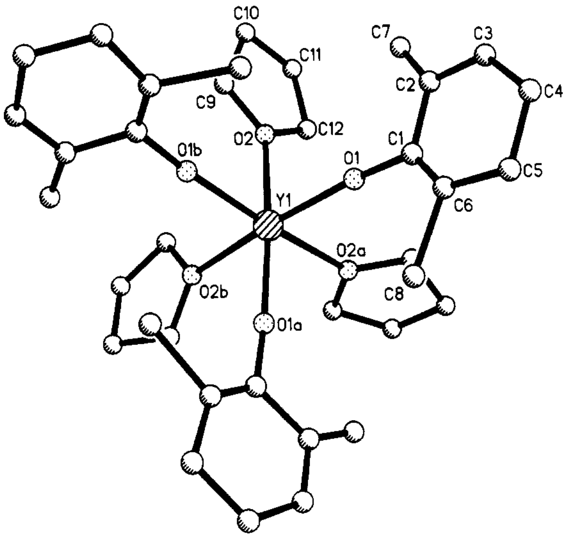

Figure 1. Molecular structure of $Y(OC_6H_3Me_2\text{-}2,6)_3(THF)_3$ (**2**).

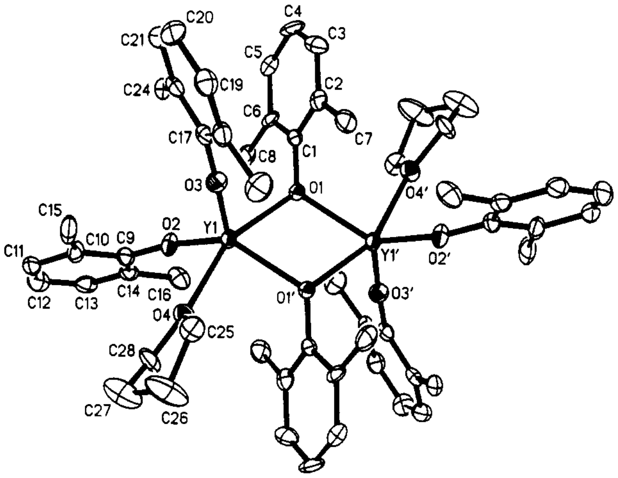

Figure 2. ORTEP diagram of $Y_2(OC_6H_3Me_2\text{-}2,6)_6(THF)_2$ (**3**) with probability ellipsoids drawn at the 40% level. Lattice toluene and hydrogen atoms are not shown.

YCl_3 (200 mg, 1.02 mmol) reacted with $NaOC_6H_3Me_2\text{-}2,6$[14] (443 mg, 3.07 mmol) in THF (18 mL) to form a cloudy solution. After the reaction mixture was stirred for 24 h and centrifuged and the solvent was removed by rotary evaporation, $Y(OC_6H_3Me_2\text{-}2,6)_3(THF)_3$ (**2**)[16] (532 mg, 78%) was obtained as a white powder, as shown in eq 1. When this white powder was

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(14) Prepared[15] from the reaction of $HOC_6H_3Me_2\text{-}2,6$ (3.95 g, 0.032 mmol), which was vacuum-distilled from CaH_2 with sodium hydride (0.930 g, 0.039 mmol) in 70 mL of THF in the dry box. After being stirred for 24 h, the slightly cloudy solution was centrifuged and the solvent was removed from the supernatant by rotary evaporation. The resulting white powder was placed under vacuum (1×10^{-4} Torr) and heated to 40 °C for 24 h. ^1H NMR (C_6D_6): δ 7.10 (d, J_{HH} = 7.3 Hz, 2 H, $OC_6\mathit{H}_3Me_2\text{-}2,6$), 6.69 (t, J_{HH} = 7.3 Hz, 1 H, $OC_6\mathit{H}_3Me_2\text{-}2,6$), 1.87 (s, 6 H, $OC_6H_3\mathit{Me}_2\text{-}2,6$). IR (KBr): 3000 w, 2965 m, 2900 s, 2845 w, 1580 s, 1460 s br, 1425 s, 1370 m, 1340 w, 1300 s br, 1080 s, 970 m, 940 w, 905 m, 845 s, 755 s, 680 m cm^{-1}.

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(16) ^1H NMR (THF-d_8): δ 6.74 (d, J_{HH} = 7.3 Hz, 6 H, $C_6\mathit{H}_3Me_2\text{-}2,6$), 6.28 (t, J_{HH} = 7.3 Hz, 3 H, $C_6\mathit{H}_3Me_2\text{-}2,6$), 2.14 (s, 18 H, $C_6H_3\mathit{Me}_2\text{-}2,6$). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 163.60 (s, $\mathit{C}_6H_3Me_2\text{-}2,6$), 129.44 (d, J_{CH} = 155 Hz, $\mathit{C}_6H_3Me_2\text{-}2,6$), 127.21 (s, $\mathit{C}_6H_3Me_2\text{-}2,6$), 116.34 (d, J_{CH} = 157 Hz, $\mathit{C}_6H_3Me_2\text{-}2,6$), 69.41 (THF), 27.50 (THF), 19.53 (q, J_{CH} = 125 Hz, $C_6H_3\mathit{Me}_2\text{-}2,6$). Anal. Calcd for $YC_{36}H_{51}O_6$: Y, 13.3. Found: Y, 13.7. IR (KBr): 3760 m, 3020 m, 2900 s br, 2700 m, 2395 m, 2000 w, 1580 s, 1250 s br, 1080 w, 760 m cm^{-1}.

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