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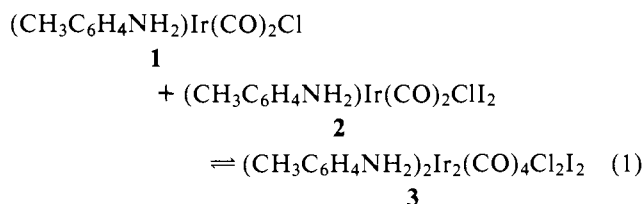
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Association of d^6 and d^8 Metal Complexes in Solution. Formation of $(p\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_2)\text{Ir}(\text{CO})_2\text{Cl}/$ $(p\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_2)\text{Ir}(\text{CO})_2\text{ClI}_2$

Sir:

Reactions between metal complexes are now realized to be of significance to a variety of chemical processes including electron transfer,¹ metal-metal bond formation in both clusters² and chain compounds,³ reductive elimination,⁴ and ligand substitution. An example of the latter class is the substitution reactions of the six-coordinate d^6 complexes of the platinum metal [particularly Pt(IV)].^{5,6} For these reactions, catalysis by planar d^8 complexes of the same metal occurs and a halo-bridged species involving the d^6 and d^8 reaction partners has been postulated as part of the reaction mechanism.⁷ However, direct observation of the halo-bridged species has not been reported.⁸ We now describe a pair of d^6 [Ir(III)] and d^8 [Ir(I)] complexes which associate in solution through a halo bridge.

Oxidation of $(p\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_2)\text{Ir}(\text{CO})_2\text{Cl}$, **1** ($\nu_{\text{C=O}}$ 2086, 2004 cm^{-1} in CH_2Cl_2 solution, 2090, 2027 in Nujol mull), which has been extensively used as a precursor of Ir(I) compounds,⁹ with an excess of iodine produces six-coordinate brown $(p\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_2)\text{Ir}(\text{CO})_2\text{ClI}_2$,¹⁰ **2** ($\nu_{\text{C=O}}$ 2151, 2105 cm^{-1} in CH_2Cl_2 solution, 2143, 2090 cm^{-1} in Nujol mull). The electronic spectra of dichloromethane solutions of mixtures of **1** and **2** show features which are not present in the spectra of the individual components. In Figure 1 the new absorption characteristic of adduct formation is seen at 490 nm. This feature develops immediately upon mixing of **1** and **2**. Analysis of the concentration dependence of this band indicates that the adduct **3** is formed via



with an equilibrium constant of 5000 (± 300) and ϵ for **3** at 490 nm of 6000 (± 300). The stability of **3** is solvent dependent. It forms in dichloromethane, chloroform, and benzene but does not form in acetone or acetonitrile. The adduct **3** may be isolated as fine green crystals¹¹ with a metallic reflectance. These may be obtained by addition of cyclohexane to a concentrated dichloromethane solution of equimolar amounts of **1** and **2** or by oxidizing **1** in dichloromethane solution with one half of a molar amount of iodine followed by crystallization through the addition of cyclohexane. The adduct **3** is diamagnetic and shows no electron spin resonance spectrum as a solid or in solution. The formation of **3** cannot be ascribed to a tendency for **1** to add ligands indiscriminately. Treatment of **1** with iodide results in substitution of iodide for chloride, but a five-coor-

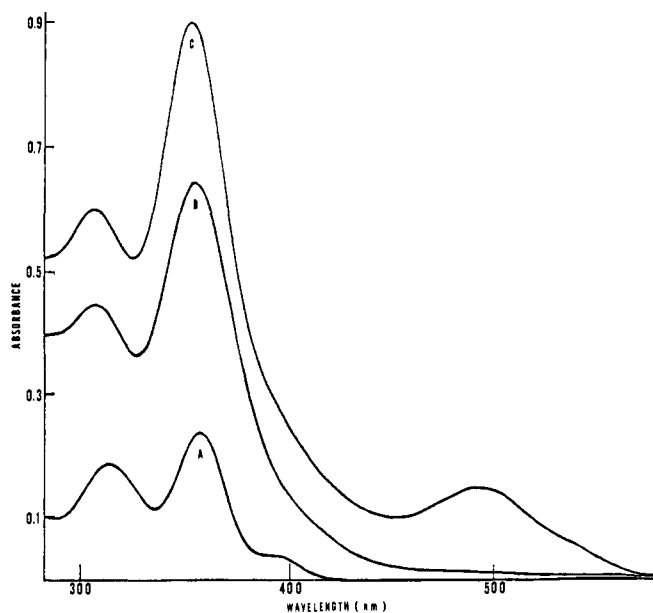
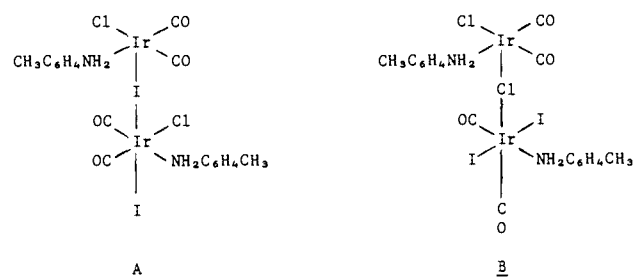


Figure 1. The electronic spectra of (a) 0.75 mM $(p\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_2)\text{Ir}(\text{CO})_2\text{Cl}$; (b) 0.75 mM $(p\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_2)\text{Ir}(\text{CO})_2\text{ClI}_2$; (c) 0.75 mM $(p\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_2)\text{Ir}(\text{CO})_2\text{Cl}$ and 0.75 mM $(p\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_2)\text{Ir}(\text{CO})_2\text{ClI}_2$. The solvent is dichloromethane throughout and the cell path length is 1.0 mm.

dinate complex is not detectable. Likewise **1** does not form an adduct with iodobenzene or chlorobenzene.

Structural information about **3** is available from its infrared spectra. In dichloromethane solutions prepared either by mixing **1** and **2** or by dissolving **3** there are no absorptions in the CO stretching region (2200–1600 cm^{-1}) other than those due to **1** and **2**. Additionally the carbonyl stretching absorptions of solid **3** as a Nujol mull (2133, 2087, 2080, 2009 cm^{-1}) occur at similar energies as were found for **1** and **2** individually. These observations eliminate the carbonyl groups as acting as bridges between the two iridium centers. Moreover, since the carbonyl stretching vibrations are sensitive to the iridium oxidation state, the data indicate that the individual iridium ions have undergone only minor perturbations in forming **3**. The data are inconsistent with the occurrence of a redox condensation to form a metal-metal-bonded Ir(II) dimer.³ Consequently we propose a halo-bridged structure, either A or B for **3** with the iodo-bridged structure A favored. **3** must derive stability from some degree of charge transfer between the two metal complexes.



The behavior of these iridium complexes contrasts to the one other system so far described in which a d^8 and d^6 pair of complexes associate in solution. In that case reaction of $\text{Rh}(\text{CNR})_4^+$ with $\text{Rh}(\text{CNR})_4\text{I}_2^+$ yields either $\text{Rh}_2(\text{CNR})_8\text{I}_2^{+2}$ or $\text{Rh}_3(\text{CNR})_{12}\text{I}_2^{3+}$ both of which have metal-metal-bonded structures.^{12–14} The factors which distinguish between halo-bridged and metal-metal-bonded structures in reactions of these types may relate to the intrinsic lability of the M-X bonds and they warrant further attention.

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References and Notes

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- (11) Anal. Calcd for $C_9H_9ClIrNO_2$: C, 20.88; H, 1.75; Cl, 6.85; I, 24.51; N, 2.71. Found: C, 20.60; H, 1.73; Cl, 6.99; I, 24.70; N, 2.60.
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Population Redistribution to Enhance NMR Sensitivity and Allow Decoupling of Low Gyromagnetic Ratio Nuclei

Sir:

The availability of the chemical information present in ^{13}C and ^{15}N NMR spectra of molecules in solution has been restricted by the poor sensitivity of these nuclei. This has motivated several approaches to transfer the relatively large magnetization of protons to nuclei possessing a low gyromagnetic ratio. The transfer of magnetization by cross-polarization (CP) has been quite successful for solids^{1,2} and has recently been demonstrated for liquids.^{3,4} Selective population transfer (SPT) between energy levels connected by proton transitions has been used to obtain enhanced signals with retention of scalar coupling.^{5,6} A new approach to SPT, known as INEPT,⁷ is based on the multiplicity and magnitude of the heteronuclear scalar coupling and not on the chemical shifts of the protons as in the standard SPT experiment. While the SPT (and INEPT) procedure increases the amplitude of the signals from the low gyromagnetic ratio nuclei, net magnetization transfer vanishes with both positive and negative signals being observed.⁵⁻⁷ Consequently, proton decoupling eliminates the signal enhancement.

To realize the advantages of both the signal enhancement of SPT and proton decoupling in a single experiment, the novel scheme outlined in Figure 1 has been developed. A series of population transfers is performed to redistribute the populations of the energy levels.⁸ The final population distribution is such that the intensities of the low gyromagnetic ratio nuclei are those of the proton transitions at equilibrium. The total time required for the magnetization transfer depends on the magnitude and multiplicity of the heteronuclear coupling.^{7,8} In the case of dioxane, an AX₂ spin system with a scalar coupling constant of 145 Hz, the entire magnetization transfer procedure requires $5/4J$ s, which is <10 ms. Since the signs of the intensities of the low gyromagnetic ratio transitions after

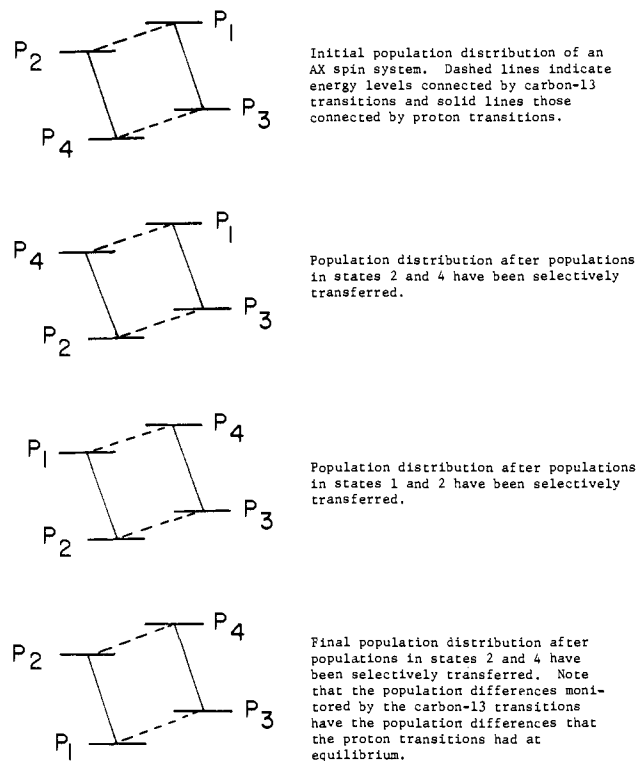


Figure 1. Outline of procedure to obtain proton-enhanced, proton-decoupled spectra. After the population transfers are completed, the population differences are sampled by obtaining a normal carbon-13 spectrum which may be proton decoupled if so desired.

the population redistribution are the same, in contrast to an SPT experiment, the free induction decay can be acquired with proton decoupling without loss of signal. Thus, this method is referred to as population redistribution for enhancement with proton decoupling (PREP).

Some typical experimental results for dioxane are shown in Figure 2. Enhancement of the carbon-13 signal by the nuclear Overhauser enhancement (NOE) is shown in Figures 2A and 2B, which compare the proton-coupled spectrum with the NOE-enhanced, decoupled spectrum. The proton-coupled spectrum obtained after the population redistribution procedure is shown in Figure 2C and the proton-decoupled spectrum in Figure 2D. It is noted that the 1:2:1 intensity pattern of the triplet is not observed in the proton-coupled spectrum after the population redistribution procedure as the magnetization transfer is from the protons to the outer energy levels of the carbon-13 transitions.⁹⁻¹² The spectra in Figures 2B and 2D were obtained in the same total time. The signal intensity obtained by the PREP method is ~40% greater than that obtained with the NOE. Since PREP is at least competitive with the commonly used NOE method for dioxane, it is of interest to compare the relative merits of the two methods as well as those of CP and SPT (see Table I).

A major drawback of the cross-polarization technique for liquids lies in the precision required in matching the Hartman-Hahn condition for efficient magnetization transfer.^{3,4} Missetting of the rf fields can lead to a severe loss in signal intensity rather than the anticipated enhancement. The SPT, PREP, and NOE methods are applicable to commercial spectrometers with adequate pulse control. The CP, SPT, and PREP methods all offer certain advantages over the NOE technique in that the pulse recycle time is governed by the proton longitudinal relaxation rate rather than that of the observed nucleus. This can lead to practical enhancements of an order of magnitude or more relative to the NOE method. The CP, SPT, and PREP methods are less dependent on the