Comparison of our results with those of Andrews and Keefer[14] on the hexamethylbenzene–I_2 complex and of Peters and Person[15] on the phenanthrene–I_2 complex (Table III) show that our values are within 1 order of magnitude of the corresponding values for these π-donor systems. In contrast, stability constant values for aminoborane–I_2 complexes reported by Eubanks and Lagowski[6] (Table III) are 2 or 3 orders of magnitude larger than our values.

We conclude that aromatic compounds incorporating B–N bonds prefer to complex with iodine by means of the π-donor interaction, rather than the stronger n-donor interaction. This suggests that the energy required to transform a planar aromatic ring to a puckered ring is too large to be offset by the formation of an n-donor bond between the nitrogen atom and I_2.

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Registry No. V, 877-07-6; VI, 15813-13-5; HMB·I_2, 81740-90-1; MBAP·I_2, 81740-91-2.

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Presence of a Substantially Bent Ir–Ir Bond in $Ir_2O(PPh_3)_2(NO)_2$

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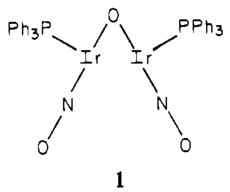
There has been much discussion of the possible existence of "bent" metal–metal bonds.[1] Calculations have confirmed the presence of metal–metal interactions in $Fe_2S_2(CO)_6$[2] and $Rh_2Cl_2(CO)_4$[3] which represent compromises between the "bent-bond" and "straight-bond" extremes, that is, between metal-orbital hybridization optimized for metal–ligand and metal–metal overlap, respectively. It has been asserted that $Co_2(CO)_8$ contains no metal–metal bond, bent or straight; the pairing of electrons leading to diamagnetism is predicted to occur in an orbital that is Co–Co antibonding (though Co–CO_{br} bonding.[4]

Among such molecules, $Ir_2O(PPh_3)_2(NO)_2$ (**1**) has long



1

Ir–Ir = 2.555 Å
∠IrOIr = 82.3°

appeared the likeliest candidate for a strong, considerably bent bond.[5] The Ir–Ir distance is shorter relative to the metal-atom radius than in those in the other complexes mentioned above. Moreover, the molecule behaves chemically as a powerful reducing agent, with accompanying structural changes interpretable as oxidative cleavage of the Ir–Ir bond. Two representative examples are shown in Scheme I.[6-8] Particularly fascinating is the unusual reduction of the N≡N– linkage in diazonium salts to an $Ir_2N{=}N-$ moiety, suggestive of the first step of N_2 reduction by the proposed sulfur-bridged Mo–Fe site in nitrogenase.[9] It is tempting to speculate that the outward projection of Ir–Ir bonding electrons by bond bending lowers activation energies for these reactions.

We undertook SCF–Xα–SW calculations[10] of $Ir_2O(PH_3)_2(NO)_2$ to clarify the nature of the Ir–Ir bonding.

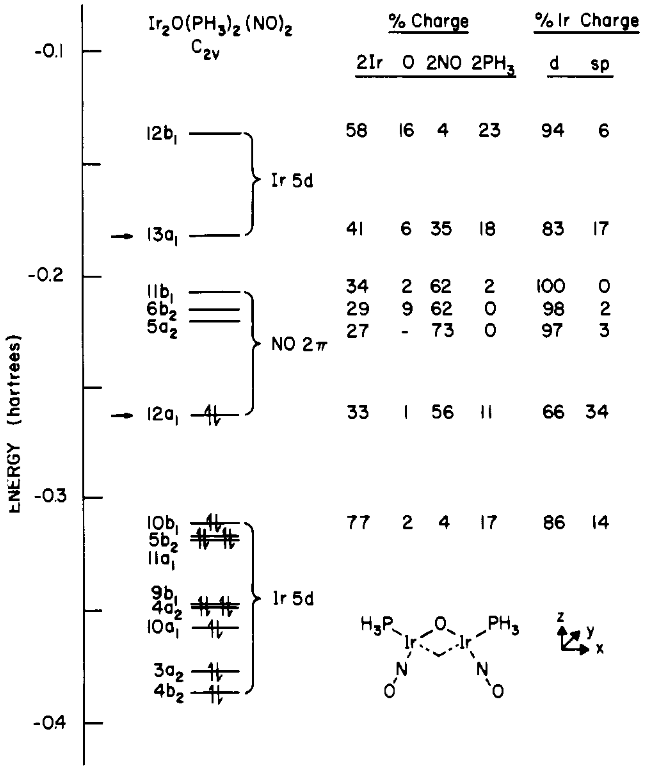
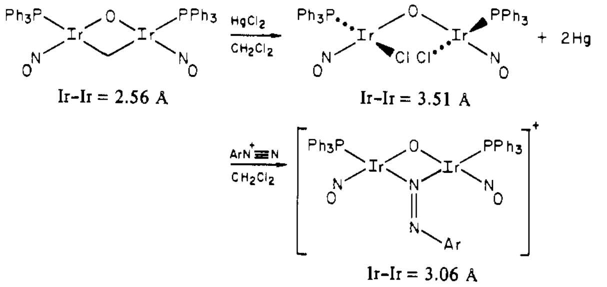


Figure 1. SCF–Xα–SW energy levels for $Ir_2O(PH_3)_2(NO)_2$ above −0.42 hartree, labeled as Ir 5d or NO 2π according to their predominant character. The exact charge distributions are given for some of the levels; that for $10b_1$ is fairly typical of the occupied 5d band. The two levels marked by arrows are those important for consideration of the nature of Ir–Ir bonding in the molecule.

Scheme I



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(10) Sphere radii, exchange parameters, etc. were chosen as in previous calculations; see, e.g., ref 3. Eighty-eight percent of the nonempirical atomic-number radii were used.

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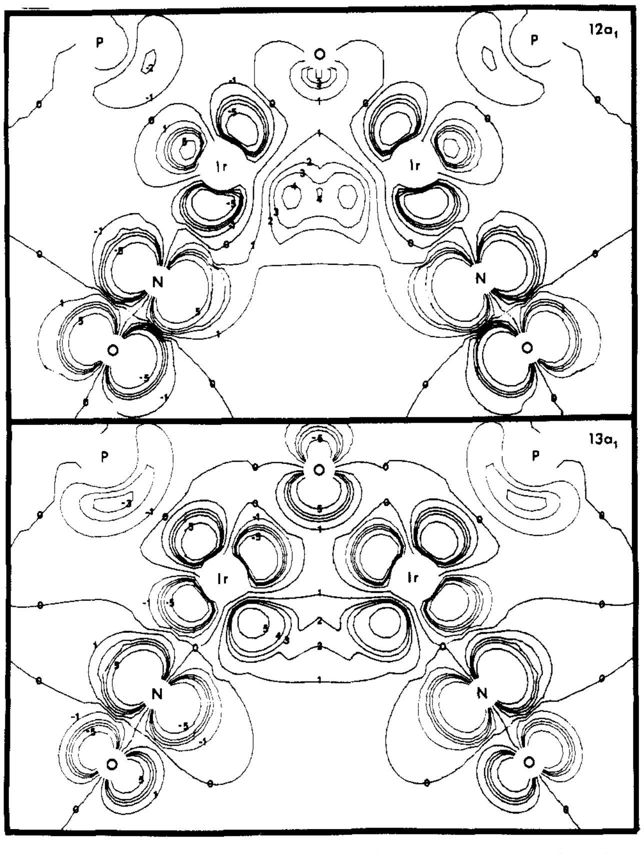

Figure 2. Contour maps of the 12a$_1$ and 13a$_1$ orbital wave functions for $Ir_2O(PH_3)_2(NO)_2$ in the molecular (xz) plane. The wave function changes sign as zero contours are crossed. A change of sign between two centers indicates an antibonding interaction; no change of sign, a bonding interaction. The contour values are 0, ±1, ±2, ±3, ±4, ±5 = 0, ±0.04, ±0.062, ±0.072, ±0.082, ±0.110 (e/bohr^3)$^{1/2}$, respectively.

Results and Discussion

Figure 1 shows our uppermost calculated energy levels and charge distributions for some of them. Not shown are lower levels of mainly O 2s and 2p, PH_3 1a$_1$, 1e, and 2a$_1$, and NO 1σ, 2σ, 3σ, and 1π character. A fundamental question in nitrosyl chemistry is whether coordinated NO is best regarded formally as NO^0 or NO^+.[11] Figure 1 indicates that the present molecule is somewhat closer to Ir^I–NO^0 than to Ir^0–NO^+. If its formation is imagined to be from $Ir_2O(PH_3)_2$ and two NO fragments, the mainly NO 2π orbitals lie between the eight filled and two empty mainly Ir–Ir 5d combinations in energy. Hence the HOMO of the molecule, 12a$_1$, has more NO than Ir character.

Comparison of individual orbital and total charge density contour maps shows, however, that the *net* in-plane Ir–Ir bonding in the molecule is essentially that arising from the 33% Ir character in the HOMO, 12a$_1$. Figure 2 shows wave function maps for 12a$_1$ and 13a$_1$. 13a$_1$ correlates with the orbital which *would* be the HOMO if the NO groups were removed. The Ir–Ir overlap in it corresponds closely to the classical bent bond which would complete square-planar coordination around each Ir. The presence of the nitrosyls, however, allows a more stable orbital to be occupied, with less Ir character but greater Ir–Ir overlap! The metal uses a 2:1 5d:6sp hybrid whose wave function lobes are slightly rotated from the fully bent toward the straight-bond alternative. As a result, the Ir–NO and Ir–PH_3 interactions are much less antibonding than in the 13a$_1$ orbital. Moreover, the larger 6s and 6p functions allow better Ir–Ir overlap: note that the contour values increase toward the center of the Ir–Ir bond in 12a$_1$, while they decrease in 13a$_1$. The resulting bond is still quite bent, more so than any other reported to date.

In summary, the unique properties of NO as a ligand—in particular, its low-lying, partially filled 2π orbitals—are crucial in stabilizing and determining the exact nature of the substantially bent metal–metal bond. Furthermore, one might expect considerable use of metal s and p orbitals to be a common feature of bent metal–metal bonds, since overlap must be achieved over fairly long distances. These conclusions may aid in future designed syntheses of bent metal–metal bonds.

It is reasonable to ask whether these results would be significantly altered by relativistic[12] and valence bond (VB)[13] corrections. Relativistic corrections, by decreasing the Ir 5d–6sp splitting,[14] should lead to better d-sp hybridization and thus increased Ir–Ir overlap. Introduction of electron correlation at the VB level should somewhat localize the 12a$_1$ electrons on the individual Ir centers. The net overlap of the two resulting VB orbitals would *probably* be less than in the MO picture. The *net* change in Ir–Ir bonding from both types of corrections is thus likely to be small, and none of the conclusions reached above should be affected.

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Registry No. $Ir_2O(PPh_3)_2(NO)_2$, 26317-79-3.

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ESR Studies of Technetium Complexes: *trans*-Aquonitrosyltetraamminetechnetium(II) and Nitrosylpentachlorotechnetium(II)

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Most technetium (Tc) complexes exhibit valence states of +5, +4, and +3.[1] The first low-valence Tc(I) cationic complex was reported by Eakins et al.[2] but formulated by them as $[Tc(NH_3OH)_2(NH_3)_3H_2O]Cl_2$. On the basis of chemical evidence and the determination of crystal structure by Radonovich and Hoard,[3] this was reformulated by Armstrong and Taube[3] as *trans*-$[Tc(NH_3)_4(NO)H_2O]Cl_2$. Technetium(I), with a 4d^6 electronic configuration, is diamagnetic. In this work, we report the observation of ESR spectra of a technetium(II) ammine complex as well as a technetium(II) pentachloro complex. To our knowledge these are the first reported room-temperature ESR spectra of the known paramagnetic low-spin d^5 technetium species.[4]

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