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Carbon Monoxide Addition to Transition Metal Complexes: Bent Metal Carbonyl Transition States

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CO is easily the most important ligand in organotransition metal chemistry. In particular, addition or loss of CO to or from a metal center is an obligatory step in many, if not most, transition metal catalyzed processes.[1] Accordingly, metal carbonyl complexes have been the subject of numerous theoretical investigations, focusing largely on the nature of the M–CO bond and on metal–carbonyl dissociation energies.[1d,2–4] However, in spite of the unique ability of computational methods to describe reaction pathways of elementary reactions, the question of the *transition state* for CO addition to unsaturated metal complexes has not been examined in detail. This is apparently because bonding in the transition state is presumed to be very weak but similar to that found in the products.[5]

Vaska's complex and its derivatives (**1**, *trans*-$IrL_2(CO)X$) bind CO reversibly (eq 1)[6] and are thus among the relatively small number of known transition metal complexes which are isolable as both the unsaturated species and their corresponding CO adducts (**2**).[7] Though this provides an ideal system for the study of various aspects of the metal–carbonyl addition/dissociation reaction, eq 1 has received less experimental attention than its H_2 counterpart.[8] Furthermore, quite surprisingly, the reaction has not, to our knowledge, been examined in detail by computational methods.

$$\underset{\textbf{1}}{\textit{trans}\text{-}\mathrm{IrL_2(CO)X}} + \mathrm{CO} \rightarrow \underset{\textbf{2}}{\textit{trans}\text{-}\mathrm{IrL_2(CO)_2X}} \qquad (1)$$

We have begun a comprehensive theoretical study of eq 1. In this communication we report the fully characterized transition state for eq 1 ($X = Cl$, $L = PH_3$), in which we find the mode of metal–CO interaction to be very different from that presented in the conventional picture of metal–carbonyl bonding. The transition-state structure exhibits a significantly bent Ir–C–O angle and may be best described as the product of a Lewis acid–base interaction in which the Ir(d_{z^2}) orbital acts as a two-electron σ-donor and an empty CO π^*-orbital acts as a σ-acceptor, i.e., σ roles opposite those in the product, **2**. The transition state for CO addition to *trans*-$Pt(PH_3)_2$ may be described similarly.

Geometry optimizations were carried out at the Hartree–Fock (HF) level[9] with the GAUSSIAN 92 series of programs,[10] using effective core potentials and at least double-ζ quality valence basis sets[11] on all non-hydrogen atoms[12] as previously described in our studies of H_2 addition to **1**.[13] The employed model satisfactorily reproduces the geometries of **1** (square planar with trans phosphines) and **2** (trigonal bipyramidal with trans phosphines)[7] and the reaction energy of eq 1 ($X = Cl$). Computed geometrical parameters of **1** ($L = PH_3$), for example, are (Å) $Ir–P = 2.331$, $Ir–Cl = 2.378$, $Ir–C = 1.811$, and $C–O = 1.159$; the respective crystallographic values ($L = PPh_3$) are 2.330, 2.382, 1.791, and 1.161.[14] The computed reaction enthalpy at this level is $\Delta H_{HF} = -9.9$ kcal/mol ($L = PH_3$) as compared to $\Delta H_{exp} = -10.8$ kcal/mol ($L = PPh_3$).[6] Additional calculations were also made on the optimized HF geometries using Møller–Plesset perturbation theory[15] carried to the MP4(SDQ) level, and basis set superposition errors (BSSEs) were corrected by the counterpoise method.[16,17]

The initial attempt to locate a transition state for eq 1 ($X = Cl$, $L = PH_3$) was carried out with the incoming carbonyl, C_iO_i, adding to **1** under a C_s symmetry constraint and with a fixed linear $Ir–C_i–O_i$ angle. Vibrational analysis of the resulting species (TS-linear) showed three normal modes with imaginary frequencies: one corresponding mainly to a relative CO translation (a′ symmetry, 158*i* cm^{-1}), one showing out-of-plane bending of the $Ir–C_i–O_i$ moiety (a″, 109*i* cm^{-1}), and one representing bending of $Ir–C_i–O_i$ in the symmetry plane of the complex (a′ symmetry, 48*i* cm^{-1}). Relaxation of the linear $Ir–C_i–O_i$ constraint removes the lowest imaginary frequency, and optimization of all geometrical parameters after removal of all symmetry constraints (C_1 point group) subsequently produces a true transition state (TS-bent) as confirmed by the presence of a single imaginary frequency at 215*i* cm^{-1}, corresponding mainly to a translation of the bent CO molecule relative to **1**. At the HF and MP4(SDQ) levels (corrected for BSSE), TS-bent is 2.5 or 5.4 kcal/mol lower in energy than TS-linear. The activation enthalpies for the formation of TS-bent are 8.5 and 4.6 kcal/mol, respectively, at these computational levels.

The geometry of TS-bent may be described as square pyramidal with the basal ligands slightly below the Ir center and the adding

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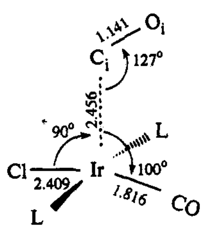
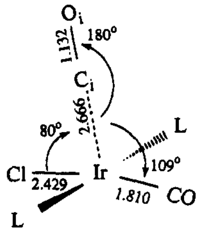


TS-bent



TS-linear

CO at the apical position forming an Ir–C_i–O_i angle, α, of 127° and a dihedral angle with the basal linear CO ligand at ca. 45°. The essential structural features in TS-bent remain intact after geometry optimization at the MP2 level of theory with Ir–C_i held fixed at its HF value (2.456 Å). In particular, the angle α optimizes to a value of 123°. As the reaction proceeds from TS-bent toward the products, the Ir–C_i–O_i angle is computed to progress quickly toward 180°. When Ir–C_i is held constant at distances successively 0.15 Å shorter than its TS-bent value (2.456 Å), energy minimizations at the HF level give respective α values of 167° (2.306 Å) and 173° (2.156 Å);[18] conversely, minimizations at longer Ir–C_i distances (2.606 and 2.756 Å) afford α values of 116° and 111°, respectively.

The stabilizing orbital interactions that can take place when a CO molecule approaches **1** with a linear Ir–CO arrangement include a σ-component involving the occupied CO(σ) and the empty Ir(p_z) orbitals and a π-component involving the nonbonding occupied Ir(d_{xz}, d_{yz}) and empty CO(π^*) orbitals. A barrier for the reaction would be attributed to the presence of a stronger antibonding interaction between the occupied CO(σ) and Ir(d_{z^2}) orbitals. Bending of the Ir–C_i–O_i moiety reduces all these interactions but allows additional bonding to take place between the occupied Ir(d_{z^2}) orbital and an empty CO(π^*) orbital with net stabilization resulting. Whereas the angle between the metal–halogen axis and the adding CO, Cl–Ir–C_i, is 90° in TS-bent, it is only 80° in TS-linear, indicating that structural rearrangements occur to reduce the repulsion between the doubly occupied Ir(d_{z^2}) and CO(σ) orbitals in TS-linear and to maximize the Ir(d_{z^2})–CO(π^*) bonding interaction in TS-bent. On the basis of this analysis, the mechanism of the CO addition reaction is best described as proceeding *via* an initial nucleophilic attack of **1** on CO (Ir(d_{z^2}) to CO(π^*) σ-donation) rather than *via* an attack by the CO lone pair on an empty metal orbital (CO(σ) to Ir(p_z)). In this context, we note that interesting ground-state analogues of TS-bent are the Vaska complex adducts of NO^+, $[Ir(PPh_3)_2(CO)(NO)(X)]^+$ (X = Cl, I), which have been crystallographically determined to contain Ir–N–O angles of ca. 125°.[19] Thus, NO^+ (isoelectronic with CO) favors electrophilic rather than nucleophilic addition to **1** even in the ground state.

Consistent with the above interpretation, the C–O bond is computed to be slightly longer (1.141 Å) in TS-bent than in free CO (computed at 1.131 Å). Additionally, a slightly negative overall charge on C_iO_i (–0.04, Mulliken population analysis) in TS-bent and a computed C_iO_i stretching frequency (2160 cm^{-1}) much smaller than in free CO (computed at 2281 cm^{-1}) can be readily interpreted as resulting from metal-to-CO electron donation. In TS-linear, C_iO_i has a bond distance of 1.132 Å, an essentially neutral charge (–0.01), and a stretching frequency (2260 cm^{-1}) comparable to that of free CO, all indicating that little, if any, charge transfer takes place to or from C_iO_i.

Using extended Huckel calculations, Hoffmann and Saillard[20] have demonstrated that two trans ligands must bend back in d^8 square planar complexes to permit oxidative addition of H_2; otherwise a large reaction barrier is encountered at even relatively long M–H_2 distances. The distortion from planarity lowers the energy of the occupied d_{z^2} orbital, thus reducing σ-repulsion, and, more importantly, raises the energy of the d_{yz} orbital which promotes metal to $H_2(\sigma^*)$ π-back-bonding. The parallel between H_2 and (linear) CO addition is well-known;[21] thus, for very similar reasons, linear CO addition to an undistorted planar complex should present a significant barrier. Further, we might expect that at long M–C distances the energy required to distort from planarity will be less than fully compensated by the weak π-interactions with an incoming CO. A square planar complex with a high-lying d_{z^2} orbital such as **1**, however, should be a good nucleophile with no need for distortion; thus we can rationalize the preference at long M–C separations for a bonding mode in which the metal acts as a σ-donor and the empty CO π^*-orbital as a σ-acceptor.

Another configuration in which the transition state for H_2 addition involves significant distortion of the trans ligands, for essentially the same reasons as above, is d^{10} *trans*-ML_2.[22] Morokuma *et al.*,[22a] for example, have found that in the transition state for H_2 addition to *trans*-$Pt(PH_3)_2$, **3**, the P–Pt–P angle is 130° or 148° depending on the approach of the H_2 molecule. Like **1**, however, **3** can act as a nucleophile toward CO without the need for distortion from linearity; indeed, the HOMOs in **3** are significantly higher in energy than those in **1**. Accordingly, in the transition state for CO addition to **3** we calculate a significantly bent Pt–C_i–O_i angle (121°), with only a minor distortion occurring in the $Pt(PH_3)_2$ moiety (P–Pt–P = 165°).

In conclusion, the transition state for CO addition to unsaturated metal centers may in some cases be best described as the result of a nucleophilic attack on CO, even when the final product is a conventional, linear, M–CO adduct. Since the mode of bonding is qualitatively different in the transition state from that in the final product, the correlation between the reaction kinetics and thermodynamics (product bond strengths) may be very poor, i.e., the Hammond postulate may not apply.[23]

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(18) These calculations reveal that as Ir–C_i decreases, the C_i–Ir–Cl angle remains fairly constant (ca. 90°) and the C_i–Ir–C (precoordinated CO) angle increases progressively, giving angles of 113° and 127° at Ir–C_i = 2.306 and 2.156 Å, respectively. The corresponding values for the C_i–Ir–P angles are 99° and 91° (in TS-bent C_i–Ir–P = 95°). While this result is consistent with an addition mechanism leading to the calculated product (trigonal bipyramidal with axial phosphines), it does not preclude the possibility that the calculated transition state might also lead to other isomeric forms of the product.

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