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Reactivity Patterns of Chromocene, Molybdenocene, and Tungstenocene Reaction Systems. I. Carbonyl Complex Formation as a Probe of Coordinative Unsaturation[1a]

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Abstract: Carbon monoxide is found to form a monocarbonyl complex with chromocene. Whereas $(C_5H_5)_2Mo(CO)$ and $(C_5H_5)_2W(CO)$ are thermally stable compounds, we find that the formation of $(C_5H_5)_2Cr(CO)$ is reversible; the associated enthalpy and entropy changes are $\Delta H_f{}^\circ = -18.8 \pm 0.5$ kcal/mol and $\Delta S_f{}^\circ = -60 \pm 2$ eu. The dicarbonyl complexes $(C_5H_5)(C_5H_7)M(CO)_2$ are stable for all three group 6 metals, M = Cr, Mo, and W. Tungstenocene, on the other hand, is unique in forming a stable dicarbonyl complex $(C_5H_5)_2W(CO)_2$ which exceeds an 18-valence-electron configuration. Factors contributing to the increasing accessibility of the metal center in the series $(C_5H_5)_2Cr$, $(C_5H_5)_2Mo$, $(C_5H_5)_2W$ to CO coordination are discussed and put in parallel to reactions of these species with other types of substrates.

Some time ago, we and others have reported on remarkable gradations in reactivity among the coordinatively unsaturated group 6 transition metal metallocenes.[2-4] Chromocene appears to be a fairly nonreactive particle, whereas both molybdenocene and tungstenocene, generated as intermediates from a number of reaction systems, will undergo a variety of basic addition and insertion steps of potential interest for homogeneous catalysis. Of the three metallocenes, however, only tungstenocene is capable of inserting into the C-H bond of aromatic hydrocarbons. In order to gain a more detailed understanding of factors contributing to this variation in reactivity, we have undertaken a systematic study of the reactions of carbon monoxide with this series of coordinatively unsaturated particles, as a particularly simple and efficient probe for coordinative unsaturation.

To date, monocarbonyl complexes have been described for molybdenocene and tungstenocene,[3,4] but not for chromocene. A stable dicarbonyl complex of composition $(C_5H_5)(C_5H_7)Cr(CO)_2$, on the other hand, has long been known to arise as one of the products when chromocene is exposed to both CO and H_2.[5] Preliminary reports on a related complex derived from molybdenocene have appeared in the literature recently.[6] We wish to report here a more systematic characterization of these known species, as well as observations on the occurrence of novel carbonyl complexes for both chromocene and tungstenocene.

Results and Discussion

1. Formation and Properties of $(C_5H_5)_2Cr(CO)$. When solutions of chromocene in petroleum ether or toluene are exposed to carbon monoxide, one observes a change in the visible spectrum. At CO pressures increasing from about 100 Torr to one atmosphere or more, one observes a diminution and final disappearance of the characteristic chromocene absorption at 454 nm. The reversibility of this reaction is established by the reappearance of this absorption band upon removal of the CO atmosphere. In a series of analogous experiments, we were unable to detect any interaction of chromocene with hydrogen gas, ethylene, 2-butyne, or diphenylacetylene.

Since complex formation is far from stoichiometric at room temperature, we have further characterized the complex formed from chromocene and carbon monoxide at lower temperatures. One finds that a petroleum ether solution of chromocene takes up CO at −78° under formation of a brownish precipitate which is stable against loss of CO in vacuo at this temperature. When warmed to room temperature, this complex loses 1 mmol of CO per millimole of chromocene; this establishes the 1:1 composition of the carbonyl complex formed. A determination of the equilibrium constant for the reaction $(C_5H_5)_2Cr$ (sol) + CO (gas) $\rightleftharpoons$ $(C_5H_5)_2Cr(CO)$ (sol) (sol = in toluene solution) is most conveniently performed by measuring the equilibrium pressure of CO (gas) over a partially carbonylated chromocene solution; measurements at different temperatures then yield the reaction enthalpy for this complex formation reaction. From the data presented in Table I we determine a standard enthalpy of complex formation of -18.8 ± 0.5 kcal/mol and an associated entropy change of -60 ± 2 eu.[7]

In the ^1H NMR spectrum of a toluene-d_8 solution of the carbonyl complex one sharp singlet is observed at τ 6.06 ppm, consistent with chemical shifts obtained with comparable, diamagnetic C_5H_5 complexes. Above 0° there is an increasing broadening of the singlet at τ 6.06, due to the re-

Table I. Equilibrium Pressure of CO, *P*(CO), and Equilibrium Constant *K* (in atm^{-1}) for the Reaction $(\eta\text{-}C_5H_5)_2Cr$ (sol) + CO (gas) $\rightleftharpoons$ $(\eta\text{-}C_5H_5)_2Cr(CO)$ (sol)

T, °K	*P*(CO), Torr	*K* (atm^{-1})
280	9.4	41.7
295	47.0	6.53
297	53.0	5.81
303	80.0	3.10
308	118.9	1.61

generation of paramagnetic chromocene. The ir spectrum of the carbonyl complex, taken in toluene solution at 0°, contains a strong, sharp carbonyl absorption at 1900 cm^{-1}. All these data clearly establish the structural analogy of $(C_5H_5)_2Cr(CO)$ to its molybdenum and tungsten homologs.

In this respect it is particularly noteworthy that in $(C_5H_5)_2Cr(CO)$, with ν(CO) 1900 cm^{-1}, one observes the lowest CO stretching frequency in the series, the corresponding values being 1921 cm^{-1} for $(C_5H_5)_2Mo(CO)$ and 1922 cm^{-1} for $(C_5H_5)_2W(CO)$.[4,8] This would indicate that electron back-donation from the metal to the CO ligand is at least as efficient for chromium as it is for its 4d and 5d homologs; hence the question arises as to why the chromocene carbonyl is so much less stable than its Mo and W homologs. Standard enthalpies of complex formation are not known for $(C_5H_5)_2Mo(CO)$ and $(C_5H_5)_2W(CO)$; these values might be estimated, however, from the thermal stability of these complexes at sublimation conditions (temperatures above 40° and pressures below 10^{-5} Torr) and from their photodecomposition by visible light, to lie between boundaries of -25 kcal/mol $> H_f° > -75$ kcal/mol. The great reduction in stability of the chromocene adduct is obviously caused by some factors other than the intrinsic metal-CO bond strengths. Since the formation of the carbonyl complex is accompanied in each case by a deformation of the axially symmetric sandwich structure, and by a pairing of two previously unpaired electrons, one is led to the conclusion that a higher spin pairing energy for chromium and/or a higher resistance of the chromium sandwich against the required structural distortion might contribute to the decreased stability of the chromocene carbonyl complex. A more quantitative estimate of these contributions will be attempted in a separate communication.[9]

2. Formation and Properties of $(C_5H_5)(C_5H_7)Mo(CO)_2$ and $(C_5H_5)(C_5H_7)W(CO)_2$. Formation of $(C_5H_5)(C_5H_7)Mo(CO)_2$ has been reported to occur when $[(C_5H_5)_2MoHLi]_4$ is treated with carbon monoxide.[6] We find that this dicarbonyl complex is obtained, more conveniently, by sodium amalgam reduction of $(C_5H_5)_2MoCl_2$ in the presence of both CO (150 atm) and H_2 (50 atm) in toluene solution at 65°. Analogously, $(C_5H_5)(C_5H_7)W(CO)_2$ is available, starting from $(C_5H_5)_2WCl_2$.

The properties of these two dicarbonyl complexes are quite similar to each other and to those reported for $(C_5H_5)(C_5H_7)Cr(CO)_2$.[5] Both $(C_5H_5)(C_5H_7)Mo(CO)_2$ and $(C_5H_5)(C_5H_7)W(CO)_2$ yield, in their ^{1}H NMR spectra, a sharp singlet at τ 5.35 ppm. Another set of resonances is observed at τ 6.37-6.50 and 8.10 ppm for $(C_5H_5)(C_5H_7)Mo(CO)_2$ and at τ 6.73 and 8.10 ppm for $(C_5H_5)(C_5H_7)W(CO)_2$. Intensity ratios of about 5:3:4 are in accord with an assignment of the singlet to a symmetric C_5H_5-ring and of the other set to allyl and methylene protons of the hydrogenated C_5H_7 ring. Similar ^{1}H NMR results have been reported for $(C_5H_5)(C_5H_7)Cr(CO)_2$.[5] Mass spectra show parent ions for $(C_5H_5)(C_5H_7)Mo(CO)_2$ and $(C_5H_5)(C_5H_7)W(CO)_2$, respectively, with correct isotope distributions. In their ir spectra, two strong and sharp, terminal carbonyl stretching absorptions are observable at 1882 and 1958 cm^{-1} for the molybdenum complex and at 1878 and 1952 cm^{-1} for the tungsten homolog. The corresponding absorptions for $(C_5H_5)(C_5H_7)Cr(CO)_2$ occur at 1835 and 1916 cm^{-1}.[5]

All three compounds $(C_5H_5)(C_5H_7)M(CO)_2$ (M = Cr, Mo, W) must contain their C_5H_7-ring as a η^3-allylic ligand, with two methylene groups out of contact with the metal, a structure similar to that reported for $(C_5H_5)(C_5H_7)Ni$.[10,11] The rather similar CO stretching frequencies indicate again that back-donation is about equally effective for all three metals, chromium causing a somewhat greater shift again to lower wavelengths. In addition, the grossly observable stability against CO dissociation does not differ between the three metals in this case, all three compounds being stable under sublimation conditions. For a first dissociation of CO from $(C_5H_5)(C_5H_7)M(CO)_2$, to form an intermediate $(C_5H_5)(C_5H_7)M(CO)$, one would not expect any significant energy contributions from an adjustment of either geometry or spin multiplicity similar to that involved in dissociation of CO from $(C_5H_5)_2M(CO)$. The C_5H_7-ring is no longer capable of coordination through more than three carbon atoms, and the primary carbonyl dissociation product would presumably still be in a spin-paired configuration. In the absence of these discriminating factors—spin pairing energies and distortion force constants—an essentially identical coordination behavior is revealed for these homologous chromium, molybdenum, and tungsten compounds.

3. Formation and Properties of $(C_5H_5)_2W(CO)_2$. In addition to the complexes described above, we have observed the formation of yet another carbonyl complex of tungstenocene, the composition of which is quite unusual, since it appears to exceed an 18-electron valence shell configuration.

When the reduction of $(C_5H_5)_2WCl_2$ is carried out under higher CO pressures in the absence of hydrogen, one obtains, instead of the green monocarbonyl formed at ambient or lower CO pressures, another complex of dark blue color. This complex exhibits in its ir spectrum two terminal CO stretching vibrations at 1872 and 1955 cm^{-1}, virtually indistinguishable from those of $(C_5H_5)(C_5H_7)W(CO)_2$. Its mass spectrum, however, contains a parent ion $[(C_5H_5)_2W(CO)_2]^+$ at *m/e* 372-366 with the correct isotope distribution, together with fragment ions $[(C_5H_5)_2W(CO)]^+$ and $[(C_5H_5)_2W]^+$, which clearly distinguish this particle from $(C_5H_5)(C_5H_7)W(CO)_2$. In addition, the ^{1}H NMR spectrum consists of only one sharp singlet with τ 4.50 ppm at temperatures between 20 and $-100°$. On the basis of these data, one can tentatively assign to this complex the composition $(C_5H_5)_2W(CO)_2$. The presence of two CO ligands would imply for this tungsten sandwich a formal 20-electron valence shell configuration. It is conceivable, however, that this complex would evade such an unfavorable situation by some distortion of the sandwich core structure toward a η^3-allylic bonding of one of the ring ligands. One would expect such a distortion to be fluxional on too fast a time scale to be detectable by an observable splitting of ring proton nuclear resonances. It is interesting to note, however, that a significant shift to lower fields is observed for the ring protons in $(C_5H_5)_2W(CO)_2$ compared to $(C_5H_5)_2W(CO)$, which might indeed be due to an unshielding of those two methine groups which are out of contact with the metal at any given time. The obvious analogy in the immediate environment of the metal in such a structure to that in $(C_5H_5)(C_5H_7)W(CO)_2$ would also provide an explanation for the virtually superimposable CO frequencies of these two compounds.

While the formation of $(C_5H_5)_2W(CO)_2$ requires the presence of elevated CO pressures, little decomposition of the complex is observed, even in solution, in the absence of

CO. Over several months, some monocarbonyl $(C_5H_5)_2W(CO)$ is regenerated in solutions of $(C_5H_5)_2W(CO)_2$, but the stability of the complex under sublimation conditions indicates that the complex retains its two CO ligands with fair rigidity; possibly, a higher oxidation state of tungsten is required as an intermediate for gain or loss of the second carbonyl ligand (cf. ref 7). We have tried to obtain, under analogous reaction conditions, the corresponding molybdenocene dicarbonyl complex. Occasionally, NMR or ir data were obtained on freshly prepared solutions, which would be in accord with the expected presence of $(C_5H_5)_2Mo(CO)_2$; only monocarbonyl $(C_5H_5)_2Mo(CO)$ was found to be present, however, after the usual work-up procedures. If the molybdenocene dicarbonyl complex $(C_5H_5)_2Mo(CO)_2$ is formed at all, it is certainly much more labile, both thermodynamically and kinetically, than its tungsten counterpart.

Conclusions

In summary, the data presented above, particularly the near-identical CO stretching frequencies observed for analogous carbonyl complexes of chromium, molybdenum, and tungsten, would indicate that these three metals impart rather similar electronic properties to their respective sandwich derivatives, and that the rather striking reactivity differences observed are certainly not exclusively and probably not even largely due to differences among the three metals in their capability for back-donation toward unsaturated ligand moieties, be it in reaction products or in transition states. On the other hand, we observe a continuous trend toward increasing accessibility of the metal to entering CO ligands in the series $(C_5H_5)_2Cr$, $(C_5H_5)_2Mo$, $(C_5H_5)_2W$. Whereas chromocene forms an unstable monocarbonyl complex only, a stable monocarbonyl complex exists for both of the heavier homologs; only tungstenocene, finally, is capable of forming even a stable dicarbonyl complex. This continuous trend reflects—among other conceivable factors—most likely a decreasing resistance of the metallocene sandwich structure against some prerequisite distortions and against the required change in spin multiplicity. This decrease in distortion force constants and electron repulsion energies in the series chromocene, molybdenocene, tungstenocene might also enter as a decisive factor into the observed differences in reactivity toward other reaction partners, such as aromatic C-H bonds. This hypothesis is to be elaborated in a subsequent communication.[9]

Experimental Section

The materials were handled under an atmosphere of argon. All solvents were distilled from appropriate drying and deoxygenation reagents in a vacuum manifold; gases were obtained in prepurified grade and used without further purification. The preparation of $(\eta\text{-}C_5H_5)_2Cr$ was based on the procedure described in ref 12. $(\eta\text{-}C_5H_5)_2MoH_2$, $(\eta\text{-}C_5H_5)_2MoCl_2$, $(\eta\text{-}C_5H_5)_2WH_2$, and $(\eta\text{-}C_5H_5)_2WCl_2$ were prepared using methods described by Green et al.[13] and Cooper and Green.[14]

1. Formation of $(\eta\text{-}C_5H_5)_2Cr(CO)$ from $(\eta\text{-}C_5H_5)_2Cr$. $(\eta\text{-}C_5H_5)_2Cr$ (298.1 mg, 1.64 mmol) was dissolved in 50 ml of petroleum ether at −78°. A brownish precipitate was observed upon introduction of 1 atm of CO. After removal of excess gas, the mixture was slowly warmed to room temperature; the evolved gases were collected via a Toepler pump, while the solution returned to its original orange color. The collected gas was identified as CO by ir. The total yield of CO corresponds to a ratio of 0.95 CO/$(\eta\text{-}C_5H_5)_2Cr$, in accord with the formation of a 1:1 complex of $(\eta\text{-}C_5H_5)_2Cr(CO)$. In the ir spectra of the brownish precipitate taken in toluene at 0°, a strong and sharp CO absorption is observed at 1900 cm^{-1}. Low temperature ^1H NMR spectra of $(\eta\text{-}C_5H_5)_2Cr(CO)$ in toluene-d_8 show a singlet at τ 6.06.

2. Equilibrium Measurements for $(\eta\text{-}C_5H_5)_2Cr + CO \rightleftharpoons (\eta\text{-}C_5H_5)_2Cr(CO)$. Chromocene (470 mg, 2.58 mmol) was dissolved in 25 ml of toluene in a flask of known volume, V, and cooled to −78°. CO gas (0.895 mmol) was introduced into this flask and allowed to react with chromocene at −78°. The system was then equilibrated at various temperatures, T, and the resulting total pressure was measured. The equilibrium pressure of CO, $P(CO)$, was obtained by correcting for the vapor pressure of toluene at that temperature. Results of duplicate experiments are given in Table I.

The equilibrium constant at each temperature was then evaluated, using the following relationship.

$$K = \frac{[(\eta\text{-}C_5H_5)_2Cr(CO)]}{[(\eta\text{-}C_5H_5)_2Cr]P(CO)} = \frac{(0.895 - N(\text{gas}))}{(2.58 - 0.895 + N(\text{gas}))P(CO)}$$

$$P(CO) = P_{\text{total}} - P_{\text{toluene}};\ P_{\text{toluene}} = \text{vapor pressure of toluene at temperature } T$$

The number of millimoles of CO in the gas phase at each temperature, N(gas), is determined from the equilibrium pressure of CO, the volume of the reaction flask, and the temperature by the ideal gas law. Values for the equilibrium constant K(atm) for the reaction $(C_5H_5)_2Cr$ (sol) + CO (gas) = $(C_5H_5)_2Cr(CO)$ (sol) are given in Table I for various temperatures. From these data, one obtains the standard enthalpy and entropy data given in section 1.

3. Preparation of $(\eta\text{-}C_5H_5)(\eta^3\text{-}C_5H_7)Mo(CO)_2$. $(\eta\text{-}C_5H_5)_2MoCl_2$ (100 mg, 0.33 mmol) and 0.7 ml of Na-Hg alloy (1 mmol of Na/ml of Hg) were suspended in 25 ml of toluene, in a side-arm flask. The mixture was stirred in the autoclave under 150 atm of CO and 50 atm of H_2 at 65° for 20 hr. The suspension was then filtered to remove sodium amalgam and NaCl. After removal of solvent, $(\eta\text{-}C_5H_5)(\eta^3\text{-}C_5H_7)Mo(CO)_2$ was obtained as an orange sublimate under a vacuum of 10^{-3} Torr at 40° (yield ca. 20%). Characterization by mass spectra, ir, and NMR spectra is as given in text.

4. Preparation of $(\eta\text{-}C_5H_5)(\eta^3\text{-}C_5H_7)W(CO)_2$. $(\eta\text{-}C_5H_5)(\eta^3\text{-}C_5H_7)W(CO)_2$ was prepared in the same manner as described for $(\eta\text{-}C_5H_5)(\eta^3\text{-}C_5H_7)Mo(CO)_2$ from $(\eta\text{-}C_5H_5)_2WCl_2$ as starting material (yield ca. 15%).

5. Preparation of $(\eta\text{-}C_5H_5)_2W(CO)_2$. $(\eta\text{-}C_5H_5)_2WCl_2$ (100 mg, 0.26 mmol) and 0.8 ml of Na-Hg (1 mmol of Na/ml of Hg) were suspended in 25 ml of toluene. The mixture was then stirred at 25° under 140 atm of CO in the autoclave for 16 hr. The suspension was filtered under Ar and the solvent was removed in vacuo. $(\eta\text{-}C_5H_5)_2W(CO)_2$ was obtained as a dark blue sublimate at 40° and 10^{-3} Torr (yield ca. 20%). For a characterization of this compound, elemental composition is practically useless; combustion analysis for C and H content could not discern this compound with sufficient reliability from either $(C_5H_5)_2W(CO)$ or $(C_5H_5)(C_5H_7)W(CO)_2$. Characterization was therefore based on mass spectra, NMR, and ir data as discussed in text.

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(1) (a) Abstracted in part from the Ph.D. Thesis of Kit L. Tang Wong, The University of Michigan, 1974; financial support of this work by the National Science Foundation (GP 33130 X), by Deutsche Forschungsgemeinschaft, and by Fonds der Chemischen Industrie is gratefully acknowledged. (b) Recipient of a Barbour Fellowship, 1972–1974. (c) Recipient of a Sloan Fellowship, 1973–1974; address correspondence to this author at Universität Konstanz.

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Reactivity Patterns of Chromocene, Molybdenocene, and Tungstenocene Reaction Systems. II. An Analysis in Terms of Molecular Orbital and Electron-Electron Repulsion Energies[1a]

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Abstract: Gradations in reactivity among the group 6 metallocenes have been studied theoretically by an extended Hückel molecular orbital analysis of one-electron energy changes associated with the formation of reaction products and intermediates, and by an evaluation of the associated electron-electron repulsion energies in terms of Racah repulsion parameters. The effect of ring-metal-ring bending distortions on spin-pairing energies is described, and the results are used to express enthalpies of formation of monocarbonyl complexes. A satisfactory accounting is obtained for the different stabilities observed for $(C_5H_5)_2Cr(CO)$ and $(C_5H_5)_2Mo(CO)$. The unique stability of the 20-electron species $(C_5H_5)_2W(CO)_2$ is discussed in terms of changes in ligand repulsions, but not thoroughly understood. The formation of the dihydride $(C_5H_5)_2MoH_2$ from a $(C_5H_5)_2Mo$ intermediate and an H_2 molecule is described in detail by a correlation diagram for various electronic states; it is concluded that the activation energy for this insertion reaction is nearly equal to the spin-pairing energy associated with its transition state. Finally, the formation of tungstenocene phenyl hydride complexes by insertion into aromatic C-H bonds is discussed in terms of repulsive ligand interactions and facilitated ring dislocations similar to those held responsible for the unique stability of the tungstenocene dicarbonyl complex mentioned above.

Interesting reactivity patterns have been established for group 6 transition metal bis(cyclopentadienyl) species with a number of substrate molecules (see Table I).

Most prominent among the reactivity differences observed is the lack of reactivity of chromocene vis-a-vis virtually all substrates except CO[2] and, on the other hand, the unique tendency of tungstenocene to form a stable dicarbonyl complex (which exceeds an 18-electron configuration)[2] and to generate phenyl hydride derivatives by insertion into aromatic C-H bonds.[3,4] In order to extract from these observations some generally useful reactivity parameters for addition or insertion reactions of low-valent metal species, we have undertaken a theoretical analysis of those factors which might govern the feasibility of reactions such as those mentioned in Table I. We wish to present here computational evidence that the reactivity differences in the series under consideration are largely due to differences in interelectronic repulsion energies, namely, one-center repulsions between d electrons on the metal atom and two-center repulsions between different ligands, which are associated with the formation of products or intermediates in the reaction concerned.

Computational Methods

The computational approach utilized in this study consists of two mutually complementary parts: an analysis of one-electron orbital energies and eigenfunctions by the extended Hückel molecular orbital (EHMO) method, and a subsequent determination of the total energies for the ensuing possible d-electron configurations and their individual multielectron states by an expansion in terms of Racah electron repulsion parameters. The role of the extended Hückel calculations is to establish values of orbital splitting and mixing associated with varying geometries. The subsequent ligand field multiplet calculations then give the energies of possible multiplet states for the various geometries of the reaction complex considered. In this way, we hope to obtain an intuitively transparent break-down of the main origins of differences in reaction enthalpies and activation barriers in this series of coordinatively unsaturated compounds.

The EHMO method has been used with considerable success in the treatment of various transition metal complexes[6-8] as well as transition states and intermediates in a variety of chemical reactions.[9-11] It has been found to yield reliable estimates of optimal geometries with respect to angular parameters,[12] since the dependence of bond angles on both overlap between bonded atoms and repulsive interaction between nonbonded atoms is appropriately modeled by this method. The EHMO program used is based on a program originally written by Hoffmann[13] and modified by Bartell et al.[14] The basis orbitals for the metal atoms are single-parameter Slater-type atomic orbitals of the np, nd, $(n + 1)$s, and $(n + 1)$p type. The np orbitals of the metal are included to provide the necessary repulsion at small internuclear metal-ligand separation. The orbital exponents and diagonal energy matrix elements adopted for the calculations are given in Table II. These values, close to those employed in earlier calculations,[6,15-17] were chosen so as to yield acceptable results on the following counts: (1) ionization potentials for both metal complexes and substrate molecules close to those experimentally determined; (2) energy gaps between occupied and empty orbitals compatible with experimentally established or supported orbital occupation