Localized Valence Structures of Transition-Metal Carbene Complexes[1]

Dennis S. Marynick* and Carol M. Kirkpatrick

Contribution from the Department of Chemistry, The University of Texas at Arlington, Arlington, Texas 76019-0065. Received September 4, 1984

Abstract: Localized molecular orbitals (LMO's) are presented for three transition-metal carbene complexes: $(CO)_5CrC$-$(CH_3)(OCH_3)$ (**1**), $(C_5H_5)(CO)_2MnC(CH_3)_2$ (**2**), and $(C_5H_5)(CH_3)TiCH_2$ (**3**). **1** exhibits a well-localized C=O double bond and a single bond between the chromium and the carbene carbon. **2** does show a Mn=C double bond, with σ–π separability. **3** exhibits a nearly nonpolar Ti–C equivalent double bond. Rotation barriers about the metal–carbon bond are calculated for all three complexes. In addition, the rotation about the C–O bond in **1** is studied.

Transition-metal carbene complexes form an important group of compounds which have been intensely studied from several viewpoints, including their synthesis,[2,3] reactivity and role in catalytic activity,[4] and molecular[5] and electronic[6] structure. These compounds may be divided into two groups, the Fischer[2] and Schrock[3] complexes. It is a curious fact that Schrock complexes (all of which have metals in high oxidation states) are nucleophilic at the carbon atom while the Fischer complexes (all of which have metals in low oxidation states) are electrophilic at the carbene carbon. In addition, it is well-known that almost all Fischer complexes have at least one heteroatom bound to the carbene carbon, with an abnormally short C–heteroatom distance (compared to that of a single bond), while the metal–carbon bond is longer than that expected for a double bond. The unusual structural and chemical properties of these systems has resulted in many theoretical studies, culminating in Taylor and Hall's (TH) comparative study of the bonding in realistic Fischer and Schrock complexes.[6a] Their view, and one with which we essentially concur, is that Fischer complexes bind datively as singlet fragments, with the π electrons polarized toward the metal; however, Schrock complexes bind covalently, with the π electrons more equally distributed between the metal and the carbene carbon. Here we report localized molecular orbital (LMO) studies of three carbene complexes: $(CO)_5CrC(CH_3)(OCH_3)$ (**1**), $(C_5H_5)(CO)_2MnC(CH_3)_2$ (**2**), and $(C_5H_5)(CH_3)TiCH_2$ (**3**). The LMO's of these systems should be of considerable interest because they represent the best *single* valence structure consistent with the molecular wave functions. In addition, we report several rotation barriers and optimized geometries for these molecules.

Calculations

All wave functions were calculated within the PRDDO approximations[7] with basis sets described previously.[8] LMO's were obtained by using the Boys criterion.[9] The experimental geometry of **1** was employed,[10] except that the Cr–C and C–O distances of the carbene were optimized. The geometry of **2** was similarly taken from experiment,[11] although the Mn–carbene distances were optimized in both conformations studied. The model Schrock complex was completely optimized except for C–H distances (fixed at 1.09 Å) and the C–C distances in the cyclopentadienyl ring (fixed at 1.40 Å). The methyl group was assumed to be tetrahedral. Although **3** is not known experimentally, titanium–carbene complexes have been postulated[12] to be intermediates in organometallic reaction mechanisms. We note here that the PRDDO method has been shown to yield excellent optimized geometries in a wide variety of transition-metal complexes,[13] reasonable conformational energies for tetracarbonyl(ethylene)iron[14] and various octahedral d^6 complexes,[15] and qualitatively correct orbital orderings for $Cr(CO)_6$ and $Ni(CO)_4$.[16]

Results and Discussion

The LMO valence structures of all three compounds are summarized in Figures 1–3. **1** exhibits a well-localized, highly polar symmetric double bond *between the carbene carbon and the oxygen* (Figure 1) with each double bond component having electron populations of 1.54 e (O) and 0.48e (C). The Cr–carbene interaction (Figure 1) is described by a single Cr–C LMO of local σ symmetry, with π back-bonding to C (from delocalized $n = 3$ metal hybrids)[17] totaling 0.21 e. The Mulliken charge on the carbene carbon is +0.06 e. Clearly our calculations indicate that the methoxy group is a better π donor than the $(CO)_5Cr$ moiety. This valence structure is entirely consistent with the long Cr–C and short C–heteroatom distances typically observed, as well as the electrophilic nature of the carbene carbon.

The optimized geometrical parameters, with experimental values in parentheses, are the following: Cr–C = 2.00A (2.04 Å[10]), C–O = 1.33A (1.33 Å[10]). Rotation of the carbene group by 90° and subsequent reoptimization of the geometry yields a barrier of 18.3 kcal/mol compared to the experimental value of 12.4 kcal/mol.[18]

(1) This is the third paper in a series of localized molecular orbital studies on transition-metal complexes. For paper II, see: Kirkpatrick, C. M.; Marynick, D. S. *J. Comput. Chem.* **1985**, *6*, 0000.

(2) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1.

(3) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.

(4) See, for instance: Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449.

(5) Schubert, U. *Coord. Chem. Rev.* **1984**, *55*, 261.

(6) (a) Taylor, T. E.; Hall, M. B. *J. Am. Chem. Soc.* **1984**, *106*, 1574. (b) Nakatsuji, H.; Ushio, J.; Han, S.; Yonezawa, T. *J. Am. Chem. Soc.* **1983**, *105*, 426. (c) Franci, M. M.; Pietro, W. J.; Hout, R. F.; Hehre, W. J. *Organometallics* **1983**, *2*, 281. (d) Kostić, N.; Fenske, R. F. *Organometallics* **1982**, *1*, 974. (e) Rappe, A. K.; Goddard, W. A. *J. Am. Chem. Soc.* **1982**, *104*, 448. (f) Spangler, D.; Wendoloski, J. J.; Dupuis, M.; Chen. M. M. L.; Schaefer, H. F. *J. Am. Chem. Soc.* **1981**, *103*, 4677. (g) Kostić, N. M.; Fenske, R. F. *J. Am. Chem. Soc.* **1981**, *103*, 4677. (h) Goddard, R. J.; Hoffmann, R.; Jemmis, E. D. *J. Am. Chem. Soc.* **1980**, *102*, 7667. (i) Kostić, N.; Fenske, R. F. *J. Am. Chem. Soc.* **1982**, *104*, 3879. (j) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585.

(7) Halgren, T. A.; Lipscomb, W. N. *J. Chem. Phys.* **1973**, *58*, 1569. Marynick, D. S.; Lipscomb, W. N. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 1341.

(8) Marynick, D. S.; Kirkpatrick, C. M. *J. Phys. Chem.* **1983**, *87*, 3273.

(9) Boys, S. F. In "Quantum Theory of Atoms, Molecules, and the Solid State"; Löwdin, P. O., Ed.; Academic Press: New York, 1966; pp 253–62.

(10) Representative geometrical parameters were taken from ref 5. The LMO's of $(CO)_5Cr(Ph)(OCH_3)$ have been calculated and are not significantly different than those of the smaller model complex discussed here.

(11) Friedrich, P.; Besl, G.; Fischer, E. O.; Huttner, G. *J. Organomet. Chem.* **1977**, *139*, C68.

(12) Juin, K. M.; Rooney, J. J.; Stewart, D. C.; Green, M. L. H.; Mahtab, A. *J. Chem. Soc. Dalton Trans.* **1979**, 262.

(13) (a) Marynick, D. S.; Axe, F. U.; Kirkpatrick, C. M.; Throckmorton, L. *Chem. Phys. Lett.* **1983**, *99*, 406. (b) Marynick, D. S., Proceedings of The Robert A. Welch Foundation Conferences on Chemical Research XXX, in press.

(14) Axe, F. U.; Marynick, D. S. *J. Am. Chem. Soc.* **1984**, *106*, 6230.

(15) Marynick, D. S.; Askari, S.; Nickerson, D. F. *Inorg. Chem.*, in press.

(16) Axe, F. U.; Marynick, D. S., unpublished results.

(17) The LMO representation of metal–ligand π bonding involves delocalized hybrids from the $n = 3$ shell of the metal: see ref 1.

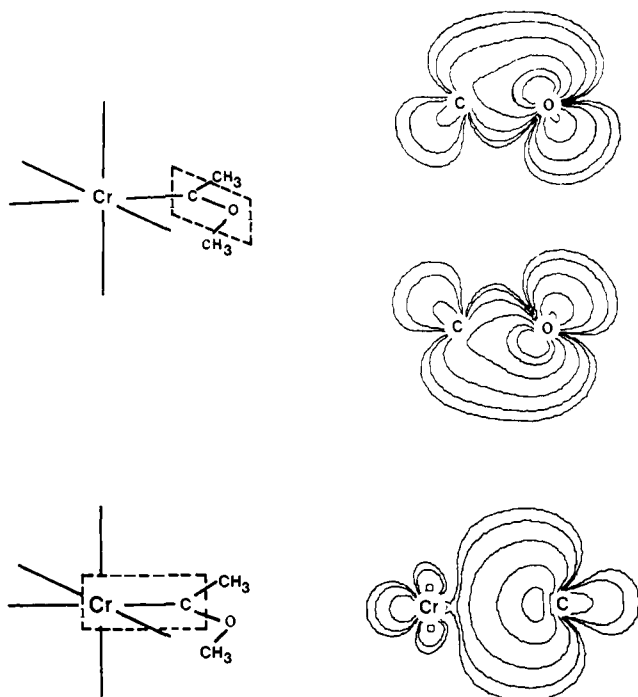(18) Kreiter, C. G.; Fischer, E. O. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 761.

Figure 1. LMO's in the C–O and Cr–C regions of (CO)₅CrC(OC-H₃)(CH₃). The planes of the contour plots are indicated in the drawings of the molecules. The top two plots are the two equivalent, highly polar C–O LMO's. The bottom plot is the dominant Cr–C σ LMO. Contour values are 0.5, 0.3, 0.1, 0.02, 0.005, and 0.002 e/au³ for these and all other plots in this paper.
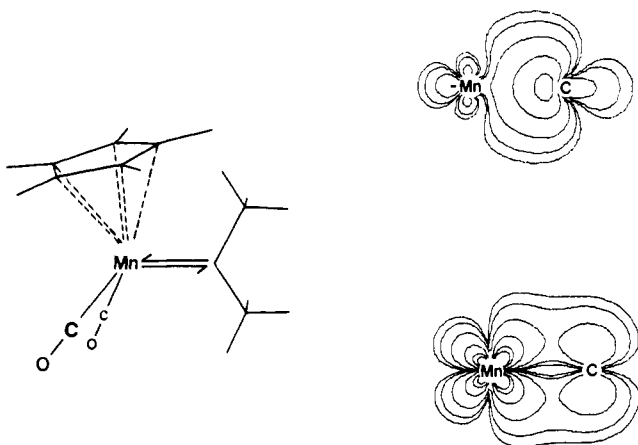

Figure 2. The σ and π LMO's in the plane containing the Mn–C axis and perpendicular to the plane of the carbene. The notation ⇋ denotes a double bond with σ–π separability.

The reoptimized geometrical parameters are Cr–C = 1.96 Å and C–O = 1.37 Å. The expected reduction of C–O and increase of Cr–C π bonding in the rotated form is evident from the change in optimized bond lengths and the LMO pattern (not shown) which now exhibits Cr–C double and C–O single bonds.

Previous calculations[6b] have indicated that rotation about the Cr–C bond is very easy, with a calculated barrier of only 0.4 kcal/mol for (CO)₅Cr=C(OH)(H). Our corresponding value is 0.7 kcal/mol. As has been pointed out previously,[6b] this barrier is not directly related to the amount of π interaction in the Cr–C bond, since a fragment analysis shows that there are two occupied "degenerate" d orbitals which allow π back-bonding in any orientation of the carbene fragment.
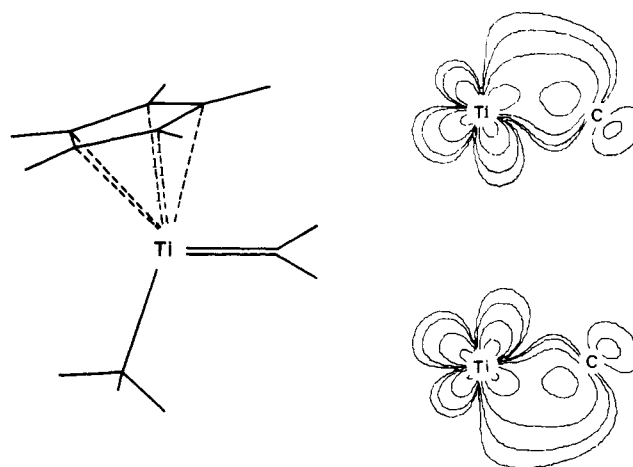

Figure 3. The two equivalent Ti–C LMO's in the plane containing the Ti–C axis and perpendicular to the carbene plane.

In marked contrast to **1**, the LMO valence structure of **2** shows (Figure 2) a well-localized Mn–C double bond, which persists even when heteroatoms are substituted for the alkyl groups on the carbene, as in (C₅H₅)(CO)₂MnC(Ph)(F) and (C₅H₅)(CO)₂Mn-C(OH)(CH₃).[19] The Mn–C double bond exhibits σ–π separability, with electron populations of 1.32 e (Mn) and 0.46 e (C) for the π component and 0.32 e (Mn) and 1.68 e (C) for the σ LMO. Thus, the (C₅H₅)(CO)₂Mn⁺ moiety has greater π donating ability than (CO)₅Cr. The internal rotation barrier for **2** has been previously estimated at 9 kcal/mol,[6i] and various rationales for the preferred conformation have been given.[6i,j] We obtain a smaller value of 1.4 kcal/mol.

The LMO's of **3** show (Figure 3) essentially equivalent Ti–C double bonds, with average electron populations of 1.05 e (Ti) and 0.96 e (C). The Mulliken charge on C is –0.21 e, consistent with the nucleophilic behavior of these types of complexes. The calculated rotation barrier about the Ti–C bond is 10.4 kcal/mol.

In summary, our LMO valence structures suggest that, while all of these complexes have significant amounts of metal–carbene π interaction, the best *single* valence structure of complexes such as **1** has only one Cr–C LMO, with a highly polar heteroatom–C double bond resulting from strong delocalization of a heteroatom lone pair to the carbene carbon. Substitution of C₅H₅⁻ for three carbonyls, as in **2**, significantly increases the π donating ability of the metal moiety and results in a Mn–C double bond with σ–π separability, even when the carbene carbon has heteroatom substituents. Only the Schrock-type complexes show nearly equivalent nonpolar double bonds similar to those found by the Boys criterion in simple organic systems such as ethylene.[20]

(19) (C₅H₅)(CO)₂MnC(OH)(CH₃) exhibits double bonds for *both* the Mn–C and C–OH interactions, resulting in five bonds to carbon. This situation, termed fractional bonding, has been discussed previously: Marynick, D. S.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1972**, *94*, 8692, Halgren, T. A.; Brown, L. D.; Kleier, D. A.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1977**, *99*, 6793.

(20) We note here that the major difference in the LMO description of **2** and **3** is *not* the disappearance of σ–π separability upon going from **2** to **3** but rather the *increase* in π bonding, resulting in a more nearly nonpolar double bond. Orbitals with local σ–π separability for **3** could easily be constructed by appropriately mixing the LMO's in Figure 3.