contributing to the reduction in structure for MEE and DEE.

Stereoplots of configurations from the simulations of liquid MEE and DEE are shown in Figures 18 and 19. The liquids are disordered with no obvious repeating polymeric units or especially favored dimer geometries. The axes of the monomer chains point in all directions so no alignment of the chains is evident. And, in keeping with dihedral angle distributions gauche bonds are rare. Coordination numbers are high in both cases and hard to estimate unequivocally. However, integrating the first peaks in $g_{OO}$ to their minima at 7.4 Å for MEE and 8.3 Å for DEE yields 12 and 13 neighbors, respectively. Thus, the number of neighbors appears to remain constant for the series which is reasonable since the size of the reference monomer (the solute) and its neighbors (the solvent molecules) are growing at the same rate.

## V. Conclusion

This work represents the most extensive theoretical treatment to date of liquid alkyl ethers. It also illustrates the quality of results and detailed insights into the structures and properties of complex organic liquids that can be obtained from statistical mechanics simulations. In this and earlier papers[4–6] it has been demonstrated that our theoretical approach is a particularly valuable means for studying internal rotation in pure liquids. The agreement between the computed and experimental thermodynamic properties for the liquid ethers including the density of DME also supports the viability of the TIPS model for representing intermolecular interactions. The additional data available from simulations in the NPT ensemble and the closer tie to the usual experimental conditions make this the procedure of choice for future work. It will be particularly interesting to study the pressure dependence of the structures, properties, and conformational equilibria for pure liquids and dilute solutions.

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# Geometry and Electronic Structure of $(CO)_3NiCH_2$. A Model Transition-Metal Carbene

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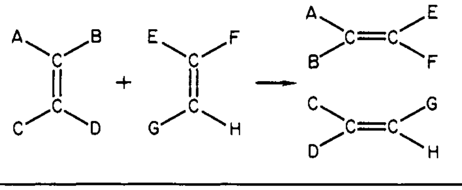
**Abstract:** The first application of nonempirical molecular electronic structure theory to a realistic transition-metal carbene complex is reported. The system chosen was $(CO)_3NiCH_2$, methylene(tricarbonyl)nickel(0). All studies were carried out at the self-consistent-field (SCF) level. A large and flexibly contracted basis set was chosen, labeled Ni(15s 11p 6d/11s 8p 3d), C,O(9s 5p/4s 2p), H(5s/3s). The critical predicted equilibrium geometrical parameters were $R$[Ni–C(methylene)] = 1.83 Å, $\theta$(HCH) = 108°. The sixfold barrier to rotation about the Ni–C(methylene) axis is small, ~0.2 kcal. The electronic structure of $(CO)_3NiCH_2$ is discussed and compared with those of the "naked" complex $NiCH_2$ and the stable $Ni(CO)_4$ molecule.

A critical ingredient in the flowering of organometallic chemistry over the past decade has been the synthesis and characterization of transition-metal carbene complexes.[1–6] This research began with the report in 1964 by Fischer and Maasböl[8] of methoxymethylcarbene(pentacarbonyl)tungsten. Although the notion of a double bond between transition metals and carbon was initially unorthodox, it is now very well entrenched and indeed an integral part of the thought patterns of organometallic researchers. In fact, metal carbene concepts borrowed from organometallic chemists are now being used in attempts to understand surface chemistry and heterogeneous catalysis.[8–12]

A primary motivation for the construction of such an analogy has been the growing consensus[13–15] that transition-metal carbenes are homogeneous catalysts in the olefin metathesis reaction.



(1)

Of the two mechanisms often considered for the olefin metathesis reactions, one involves the pairwise exchange between two olefins in the coordination sphere of a metal, while the other is the "carbene chain reaction" in which a carbene–metal complex is the active catalyst. Experimentally, isomerization patterns and

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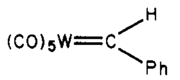
0002-7863/81/1503-3985$01.25/0

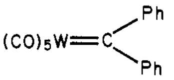
Table I. Ni Atom Basis Set Designated Ni(15s 11p 6d/11s 8p 3d)

| type | orbital exponent α | contraction coeff |
|---|---|---|
| s | 284878.0 | 0.00032 |
| | 41997.9 | 0.00246 |
| | 9627.67 | 0.01254 |
| | 2761.96 | 0.04926 |
| | 920.488 | 0.14950 |
| s | 341.805 | 1.0 |
| s | 138.023 | 1.0 |
| s | 59.2587 | 1.0 |
| s | 20.3712 | 1.0 |
| s | 8.5940 | 1.0 |
| s | 2.39417 | 1.0 |
| s | 0.918169 | 1.0 |
| s | 0.346 | 1.0 |
| s | 0.130176 | 1.0 |
| s | 0.046392 | 1.0 |
| p | 1774.18 | 0.00295 |
| | 423.403 | 0.02337 |
| | 138.311 | 0.10406 |
| | 53.1703 | 0.28226 |
| p | 22.3874 | 1.0 |
| p | 9.92848 | 1.0 |
| p | 4.11625 | 1.0 |
| p | 1.71031 | 1.0 |
| p | 0.672528 | 1.0 |
| p | 0.264 | 1.0 |
| p | 0.104 | 1.0 |
| d | 48.9403 | 0.02706 |
| | 13.7169 | 0.14598 |
| | 4.63951 | 0.36418 |
| | 1.57433 | 0.46438 |
| d | 0.486409 | 1.0 |
| d | 0.1316 | 1.0 |

isotope scrambling ratios are utilized to decide between alternative mechanisms. Some of the most important work in pinning down the role of molecules such as


$\mathrm{(CO)_5W{=}C}\begin{smallmatrix}\mathrm{H}\\\mathrm{Ph}\end{smallmatrix}$

and


$\mathrm{(CO)_5W{=}C}\begin{smallmatrix}\mathrm{Ph}\\\mathrm{Ph}\end{smallmatrix}$

as catalysts for (1) has been reported by Casey,[16,17] Grubbs,[18] and Katz.[19]

From a theoretical perspective, the simplest realistic transition-metal carbene might involve only CO ligands and the primitive $CH_2$ or methylene itself. Furthermore, such prototype carbene complexes should fulfill the 18-electron rule.[20] In this light, it becomes apparent that the simplest model transition-metal carbenes of this type are methylene(pentacarbonyl)chromium(0)

$$(CO)_5Cr{=}CH_2$$
**1**

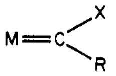
methylene(tetracarbonyl)iron(0)

$$(CO)_4Fe{=}CH_2$$
**2**

and methylene(tricarbonyl)nickel(0)

$$(CO)_3Ni{=}CH_2$$
**3**

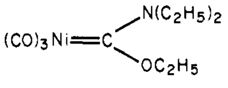
None of these three molecules has been prepared to date in the laboratory, primarily because of the problems involved in incorporating the unsubstituted methylene as a ligand. In fact, the only organometallic complex thus far reported with an $M{=}CH_2$ bond is Schrock's $Cp_2TaCH_3CH_2$ molecule,[21] which appeared in 1975. That is, the common metal–carbene complexes are the Fischer-type carbenes[1,3] of the general type


$\mathrm{M{=}C}\begin{smallmatrix}\mathrm{X}\\\mathrm{R}\end{smallmatrix}$

**4**

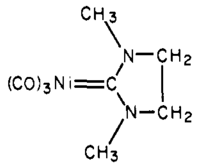
where X is an alkoxy group OR or amino group $NR_2$.

In the present paper, we report a detailed theoretical study of the simplest of the three prototypes **3**. Not only is this the first ab initio investigation of a realistic metal–carbene complex, it is also one of the very few studies[22,45,46] [see, for example, the recent work on $Ni(C_2H_4)_3$] of any organometallic species using a large and flexibly contracted basis set. Before closing this introduction, we should note that relatively few nickel–carbene complexes have been prepared.[23-28] Among these, the most closely related to $(CO)_3Ni{=}CH_2$ are Fischer's molecule[23]


$\mathrm{(CO)_3Ni{=}C}\begin{smallmatrix}\mathrm{N(C_2H_5)_2}\\\mathrm{OC_2H_5}\end{smallmatrix}$

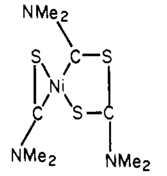
**5a**

and the



**5b**

complex of Lappert and Pye.[26] Apparently, the only nickel carbene for which a crystal structure[27] has been determined is the more complicated $[Me_2NCSNiC(NMe_2)SC(NMe_2)S]^+$ (dimethylthiocarboxamide-*C,S*)[(dimethylamino)(dimethyldithiocarbamato)carbene-*C,S*]nickel(II) ion:



**5c**

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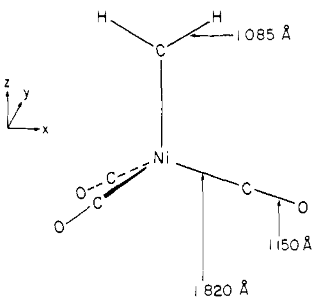

**Figure 1.** Structural assumptions for the prototype nickel-carbene complex. The three CO ligands are assumed to be tetrahedrally coordinated about the nickel atom.

This compound has a Ni=C bond distance of 1.909 Å and is remarkably stable, with samples of its salts being exposed to air for periods of several months without apparent decomposition. Thus, while the $(CO)_3Ni{=}CH_2$ complex is not expected to be terribly stable, it should be a "makable" molecule.

## Assumptions, Basis Sets, and Naked $Ni{=}CH_2$ Results

The theoretical results reported in this work were obtained by the single-configuration, closed-shell, self-consistent-field method. The geometrical optimizations were of a limited nature and intended to characterize only the $Ni{=}CH_2$ interaction.

The basis set used in this study included a large Ni-atom basis that is closely related to those recently used by Hood, Pitzer, and Schaefer[34] for $NiH_4$ and Pitzer and Schaefer[22] for $Ni(C_2H_4)_3$. To the Wachters[33] (14s 9p 5d) set we have added (a) an s function with $\alpha = 0.346$ to span the considerable space between the 3s- and 4s-like primitive Gaussian functions, (b) two sets of p functions ($\alpha$ = 0.264, 0.104) to span the Ni 4p orbital space, and (c) a set of d functions ($\alpha$ = 0.1316)[35] to expand the size of the atomic nickel 3d orbital.[35-38] As shown in Table I, the above basis set involves a very flexible contraction and may be labeled[38] Ni(15s 11p 6d/11s 8p 3d). For completion of the basis set, the Huzinaga–Dunning (9s 5p/4s 2p) set[39] for C and O and the (5s/3s) set[40] for hydrogen were appended.

With the above basis set, the two critical SCF equilibrium geometrical parameters for $^1A_1$ $NiCH_2$ are predicted to be

$$R_e(\text{Ni–C}) = 1.743\ \text{Å}, \qquad \theta_e(\text{HCH}) = 111.6° \tag{2}$$

with a total energy of −1545.59754 hartree.

Further extensions of the basis set, using Dunning's (10s 6p/5s 3p) basis of carbon and including a set of polarization functions on carbon, did not affect the geometry significantly.

This structure agrees with the structure predicted by Rappe and Goddard,[31] $R_e$(Ni–C) = 1.78 Å and $\theta_e$(HCH) = 113.7°, using the generalized valence bond approach in conjunction with effective potentials.

The small difference with their results can be attributed to (a) their use of an effective potential for the nickel core electrons and/or (b) the neglect of correlation effects in the present work.

## Study of the $(CO)_3NiCH_2$

From the study of the $NiCH_2$ it appears that the basis set described previously should provide results close enough to the Hartree–Fock limit to allow us to ascribe remaining problem to the effects of electron correlation. However we feel that electron correlation is unlikely to affect to a significant degree the geometrical structure of this closed-shell system satisfying the 18-electron rule.

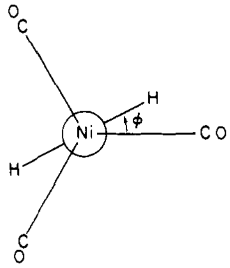

**Figure 2.** Definition of the angle $\phi$ describing the rotation of the methylene group in $(CO)_3NiCH_2$. The eclipsed conformation is $\phi$ = 0° and the staggered conformation $\phi$ = 30°.

The determination of the geometrical parameters $R$(Ni–C) and $\theta$(HCH) characterizing the $Ni{=}CH_2$ interaction was carried out with the three CO ligands in $(CO)_3Ni{=}CH_2$ constrained to the tetrahedral arrangement found experimentally[29] by Brockway and Cross for the related $Ni(CO)_4$ molecule. Furthermore, each of the Ni–C(carbonyl) distances was constrained to 1.820 Å, while each C–O distance was similarly fixed at 1.150 Å. These constraints are illustrated in Figure 1.

The optimized Ni=C distance was found to be 1.831 Å and the angle $\theta$(HCH) to be 108.2°. Further calculations to investigate the coupling between $R$(Ni–C) and $\theta$(HCH) did not affect these two equilibrium geometrical parameters.

A comparison of our predicted $(CO)_3NiCH_2$ structure with the known nickel carbene crystal structure (5C) indicates that the calculated Ni=C bond length of 1.831 Å is in reasonable agreement with the experimental Ni=C distance of 1.909 Å. In fact, the shorter distance for the prototype nickel–carbene complex studied here suggests a stronger double bond than in the experimentally prepared complex. As for the HCH bond angle, the comparison is not meaningful since the NCS angle in (**5c**) is attached to a five-membership ring.

A comparison between the structures of $(CO)_3NiCH_2$ and that of the naked $NiCH_2$ molecules show that the structures are very similar. In $NiCH_2$, the Ni=C bond is 0.088 Å shorter and the HCH angle 3.4° larger than in the carbonyl complex, suggesting a stronger bond in the naked molecule.

The geometrical optimization described earlier assumed a staggered conformation (see Figure 2). The eclipsed conformation corresponds to the angle $\psi$ = 0°. The system has a sixfold rotational barrier; i.e., when the angle $\psi$ reaches 60°, the rotational function begins to repeat itself. With $R$(Ni=C) fixed at 1.831 Å and the HCH angle of 108.2°, the eclipsed conformation has an energy higher than the staggered conformation by 0.16 kcal/mol.

A small (~0.2 kcal/mol) sixfold barrier with a minimum at the staggered form and maximum at the eclipsed form is consistent with both chemical intuition and simpler theoretical methods. For example, Albright, Hoffmann, Tse, and D'Ottavio,[41] using qualitative molecular orbital theory, recently examined a series of rotational barriers in acyclic and cyclic polyene $-ML_2$ and $-ML_4$ complexes. They found small barriers in cases (analogous to the present) where a twofold rotor is pitted against a threefold or higher rotor.

## Study of $Ni(CO)_4$

To test the reliability of the above structural predictions, the geometry of the known $Ni(CO)_4$ molecule was optimized. Si-

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Table II. Selected Mulliken Population for the Prototype Nickel-Carbene Complex and Two Related Molecules

| | $NiCH_2$ | $(CO)_3NiCH_2$ | $Ni(CO)_4$ |
|---|---|---|---|
| | | Ni[a] | |
| s | 6.05 (5.96) | 6.04 (6.14) | 6.06 (6.16) |
| p | 12.18 | 12.61 | 12.58 |
| d | 9.18 (9.27) | 8.82 (8.72) | 9.13 (9.03) |
| total | 27.40 | 27.47 | 27.77 |
| | | Methylene C | |
| s | 3.49 | 3.58 | |
| $p_x$ | 1.01 | 0.47 | |
| $p_y$ | 1.02 | 1.05 | |
| $p_z$ | 1.33 | 1.48 | |
| total | 6.85 | 6.58 | |
| | | H | |
| s | 0.87 | 0.85 | |
| | | Carbonyl C | |
| s | | 3.60, 3.65, 3.65 | 3.67 |
| p | | 2.28, 2.27, 2.27 | 2.23 |
| total | | 5.89, 5.92, 5.92 | 5.90 |
| | | O | |
| s | | 3.80, 3.80, 3.80 | 3.79 |
| p | | 4.38, 4.38, 4.38 | 4.37 |
| total | | 8.17, 8.17, 8.17 | 8.15 |

[a] Parentheses enclose the Ni s and d populations when the three basis functions of the type $(x^2 + y^2 + z^2)f(r)$ are included with the other five d functions. In fact, these three functions are 3s-like and belong properly with the other eleven Ni s functions.

Table III. Core Orbital Energies of $NiCH_2$, $(CO)_3NiCH_2$, and $Ni(CO)_4$

| atomic description | $NiCH_2$ | | $(CO)_3NiCH_2$ | | $Ni(CO)_4$[a] | |
|---|---|---|---|---|---|---|
| 1s Ni | $1a_1$ | −305.4937 | 1a′ | −305.5058 | $1a_1$ | −305.4489 |
| 2s Ni | $2a_1$ | −37.7841 | 2a′ | −37.8106 | $1a_1$ | −37.7423 |
| 2p Ni | $1b_2$ | −32.8210 | 3a′ | −32.8478 | $1t_2$ | −32.7706 |
| 2p Ni | $1b_1$ | −32.8206 | 4a′ | −32.8327 | | −32.7706 |
| 2p Ni | $3a_1$ | −32.7935 | 1a″ | −32.8312 | | −32.7706 |
| 1s O | | | 5a′ | −20.6854 | $3a_1$ | −20.6863 |
| 1s O | | | 6a′ | −20.6816 | $2t_2$ | −20.6863 |
| 1s O | | | 2a″ | −20.6816 | | −20.6863 |
| 1s O | | | | | | −20.6863 |
| 1s C | $4a_1$ | −11.1796 | 7a′ | −11.4311 | $4a_1$ | −11.4265 |
| 1s C | | | 3a″ | −11.4237 | $3t_2$ | −11.4265 |
| 1s C | | | 8a′ | −11.4237 | | −11.4265 |
| 1s C | | | 9a′ | −11.2718 | | −11.4265 |
| 3s Ni | $5a_1$ | −4.7527 | 10a′ | −4.7607 | $5a_1$ | −4.6990 |
| 3p Ni | $2b_2$ | −3.1646 | 11a′ | −3.1668 | $4t_2$ | −3.1023 |
| 3p Ni | $2b_1$ | −3.1554 | 4a″ | −3.1566 | | −3.1023 |
| 3p Ni | $6a_1$ | −3.1352 | 12a′ | −3.1551 | | −3.1023 |

[a] Orbitals of similar atomic percentage are collected together.

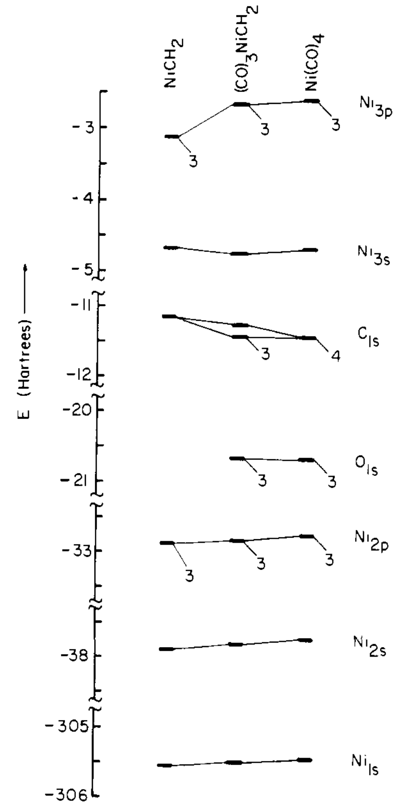

Figure 3. Core orbital energies of $NiCH_2$, $(CO)_3NiCH_2$, and $Ni(CO)_4$. Orbitals of similar atomic parentage are linked together.

multaneous optimization of the bond lengths assuming $T_d$ symmetry and using the same basis set yielded an Ni–C distance of 1.884 and a C–O distance of 1.139 Å, for a total energy of −1957.493611 hartree compared to the recent electron diffraction results of Hedberg et al., Ni–C = 1.838 and C–O = 1.141 Å. The agreement is satisfactory. Using results for molecules containing first-row atoms as a guide, we anticipate that d functions on carbon and f functions on nickel would reduce the theoretical distance to a value closer to experiment.

We can now make some comparisons between the overall Mulliken populations (given in Table II) of $Ni(CO)_4$ and $(CO)_3NiCH_2$. It should be emphasized that while any given Mulliken atomic population is of questionable absolute value, the use of the same basis set and the same SCF procedure for the three molecules studied here should make comparisons significant.[44]

The larger positive charge on Ni in the carbene complex as opposed to $Ni(CO)_4$ is seen to be due to the negative charge (0.58) buildup on the electrophilic methylene carbon. This increased methylene carbon population resides to a high degree in the methylene p orbitals. The latter hold 3.00 Mulliken electrons, compared with only 2.22 for the carbon p orbitals of each C atom in $Ni(CO)_4$. In this Mulliken picture the carbonyl carbons are consistently slightly positive (~+0.1) in both $(CO)_3NiCH_2$ and $Ni(CO)_4$, and their populations differ relatively little between the two molecules. There is, however, a slight shift from carbon s to p populations in the carbene complex relative to $Ni(CO)_4$.

The dominant difference between the Ni atom charge distributions in $(CO)_3NiCH_2$ and $Ni(CO)_4$ is seen to lie with the 3d populations. The carbene complex has a population of 8.72 d electrons, while $Ni(CO)_4$ has 9.03. The difference, 0.31 $e^-$, is remarkably close to the difference of 0.29 obtained by subtracting the total Ni charges $Ni^{+0.53}$(carbene) $-Ni^{+0.24}$(tetracarbonyl).

It is worth noting that while both $(CO)_3NiCH_2$ and $Ni(CO)_4$ are commonly referred to as $d^{10}$ complexes, it is the Ni 4s and 4p which play an important role in the metal–ligand bonds. After the 12 electrons occupying the Ni 2p and 3p orbital are discounted, there are still 0.61 and 0.58 $e^-$ occupying p functions for the two molecules. This ~0.6 electron can be attributed to nickel 4p participation, which is seen to be quite important. Certainly for the two molecules under discussion, 4p participation is much more important than 4s.

## Comparison between Core Orbitals

The lower orbital energies [ionization potentials (IP) via Koopmans' theorem) are given in Table III for all three molecules, $NiCH_2$, $(CO)_3NiCH_2$, and $Ni(CO)_4$. They are the orbitals which

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(44) (a) One of the endemic problems of transition-metal complex calculations is that the Mulliken population of individual atomic orbitals can sometimes be fairly large and negative! For a detailed discussion of this problem, see papers by: Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffman, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686. (b) Whangbo; M.-H.; Hoffman, R. *J. Chem. Phys.* **1978**, *68*, 5498. In $(CO)_3NiCH_2$, for instance, the population of one of the s orbitals is −0.28. This obvious shortcoming is avoided by using the Löwdin population analysis scheme, but because the bulk of previous work has been with the Mulliken scheme, we have also used it in this paper.

(45) Demuynck, J.; Strich, A.; Veillard, A. *Nouv. J. Chim.* **1977**, *1*, 217.

(46) Noell, J. O.; Morokuma, K. *Inorg. Chem.* **1979**, *18*, 2774.

**Table IV.** Valence Orbital Energies of $NiCH_2$, $(CO)_3NiCH_2$, and $Ni(CO)_4$

| $NiCH_2$ | | $(CO)_3NiCH_2$ | | $Ni(CO)_4$ | |
|---|---|---|---|---|---|
| | | 13a′ | −1.5528 | $6a_1$ | −1.5622 |
| | | 14a′ | −1.5493 | $5t_2$ | −1.5620 |
| | | 5a′ | −1.5491 | | −1.5620 |
| | | | | | −1.5620 |
| | | 15a′ | −0.9012 | $7a_1$ | −0.8240 |
| $7a_1$ | −0.8270 | 16a′ | −0.8233 | $6t_2$ | −0.8092 |
| | | 17a′ | −0.8085 | | −0.8092 |
| | | 6a″ | −0.8075 | | −0.8092 |
| | | 18a′ | −0.6927 | $8a_1$ | −0.6883 |
| | | 7a″ | −0.6604 | 1e | −0.6623 |
| | | 19a′ | −0.6597 | | −0.6623 |
| | | 8a″ | −0.6593 | $7t_2$ | −0.6598 |
| | | 20a′ | −0.6555 | | −0.6598 |
| | | 21a′ | −0.6491 | | −0.6598 |
| | | 9a″ | −0.6484 | $1t_1$ | −0.6517 |
| | | 22a′ | −0.6432 | | −0.6517 |
| | | 10a″ | −0.6430 | | −0.6517 |
| $8a_1$ | −0.5930 | 11a″ | −0.5873 | $8t_2$ | −0.6334 |
| $3b_2$ | −0.5575 | 23a′ | −0.5432 | | −0.6334 |
| $1a_2$ | −0.5231 | 12a″ | −0.5199 | | −0.6334 |
| $9a_1$ | −0.5064 | 24a′ | −0.4822 | 2e | −0.4444 |
| $4b_2$ | −0.4751 | 13a″ | −0.4241 | | −0.4444 |
| $10a_1$ | −0.3448 | 25a′ | −0.3604 | $9t_2$ | −0.3785 |
| $3b_1$ | −0.2707 | 26a′ | −0.3214 | | −0.3785 |
| | | | | | −0.3785 |

qualitatively correspond to atomic 1s, 2s, 2p, 3s, and 3p on Ni and 1s on C and O. These results were obtained at the respective computed equilibrium geometries. The orbital energies in Table III have been arranged to facilitate comparisons between the three molecules and have also been displayed in Figure 3.

Since $(CO)_3NiCH_2$ has one less oxygen atom than $Ni(CO)_4$, there is essentially a one-to-one correspondence between the core orbital energies. Perhaps the most obvious difference is that the atomic nickel-like $\epsilon$'s for the carbene complex are uniformly lower. Specifically, these differences are (in eV) 1.5 (1s), 1.9 (2s), 2.1, 1.7, and 1.6 (2p), 1.7 (3s), 1.8, 1.5, and 1.4 (3p). The traditional interpretation of such results would be that the higher ionization potentials of the Ni core levels of the carbene complex are indicative of a greater positive charge on the Ni atom there than in the $Ni(CO)_4$ molecule. Table II, giving the Mulliken atomic populations, does show that the Ni atom charge in the carbene complex is +0.53, notably greater than the +0.24 found for nickel tetracarbonyl. Although both molecules are formally designated zerovalent [i.e., Ni(0)], it is clear that more electron density has been removed from the vicinity of the Ni atom in the carbene complex than in $Ni(CO)_4$. The consistency in this respect with the predicted ionization potentials is encouraging.

Another interesting feature of the orbital energies given in Table III is the splitting of the $Ni(CO)_4$ degeneracies induced by replacement of one CO by a methylene. For example, the triply degenerate $1t_2$ orbital of $Ni(CO)_4$ is split into 3a′, 4a′, and 1a″ orbitals for $(CO)_3NiCH_2$. The separation between the 3a′ and 1a″ orbital energies (Koopman's theorem ionization potentials) is 0.45 eV. Similarly, the $4t_2$ orbital of $Ni(CO)_4$ splits into 11a′, 4a″, and 12a′ orbitals of the carbene complex, with a separation $\epsilon(11a') - \epsilon(12a') = 0.32$ eV. In contrast to these splittings, the oxygen 1s and 2s orbitals which are degenerate in $Ni(CO)_4$, namely, the $2t_2$ and $5t_2$ orbitals, remain essentially degenerate in $(CO)_3NiCH_2$.

The most obvious nontrivial differences between the $Ni(CO)_4$ and $(CO)_3NiCH_2$ IP's involve the methylene carbon atom. This is hardly surprising, since the electronic environment at carbon is quite different for $CH_2$ than for CO. These differences may be very helpful in identifying the photoelectron spectrum of $(CO)_3NiCH_2$ or related carbene complexes. For example, the carbon 1s IP (9a′) associated with methylene is approximately 4 eV less than the 1s IP's (7a′, 3a″, 8a′) associated with carbonyl. When the orbital eigenvalues are plotted as in Figure 3, it is quite clear that the former are energetically closer to the 1s carbene IP of $NiCH_2$, while the latter are closer to the 1s (carbonyl) IP of $Ni(CO)_4$. As with the Ni core levels, the difference can once again be attributed to the greater negative charge on methylene vs. carbonyl.

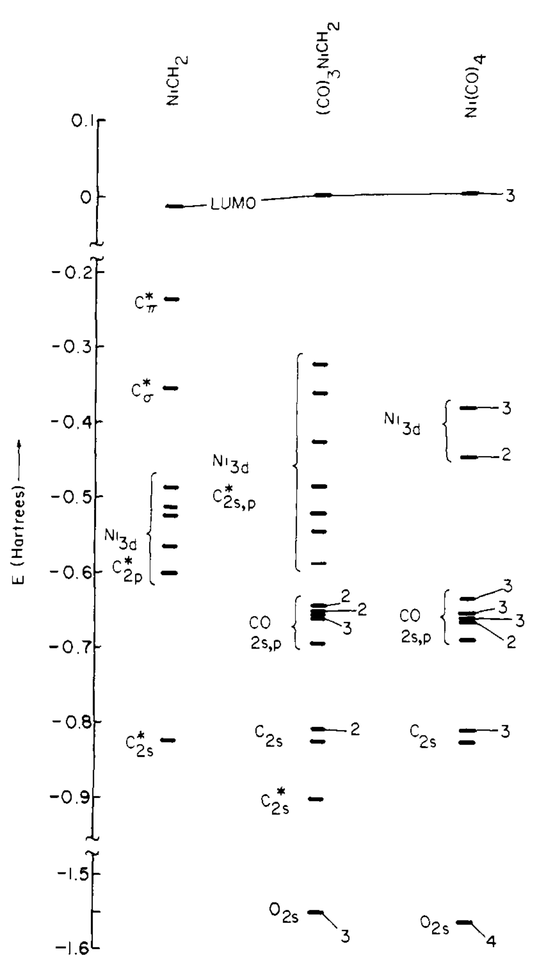

**Figure 4.** Valence orbital energies of $NiCH_2$, $(CO)_3NiCH_2$, and $Ni(CO)_4$.

## Comparison between Valence Orbitals

Most of the chemical properties of the $NiCH_2$, $(CO)_3NiCH_2$, and $Ni(CO)_4$ molecules are expected to be determined by the nature of their higher occupied and lower unoccupied molecular orbitals. The former are collected in Table IV. The energies of these valence orbitals are also displayed in Figure 4 where they have been labeled somewhat arbitrarily by their dominant components. As with the atomic core orbitals discussed previously, the energetically remote oxygen 2s orbital energies are relatively constant in both complexes. The carbon 2s orbitals in $(CO)_3NiCH_2$, however, are markedly different for carbene vs. carbonyl, and this is not surprising as it is now no longer valid to think in atomic orbital terms, since these valence orbitals have strong interatomic overlaps and interaction. What is perhaps more significant is that the carbene 2s is lower in energy compared to the carbonyl 2s—quite the opposite of what one might expect by looking at the net charges on the carbon atoms and the relative energies of the C 1s levels. This is because the energies of valence levels, unlike the core, are largely determined by their interactions with closely neighboring atoms and not by their general electrostatic environments. The fragment orbitals appear to retain the charge effect, for the carbene 2s level in $NiCH_2$ is higher than the carbene 2s in $(CO)_3NiCH_2$ as would be expected from the greater negative charge on the carbon in the former complex.

The nickel d orbitals are recognizable in $NiCH_2$ and the tetracarbonyl complex, but in $(CO)_3NiCH_2$ they become intimately mixed with the $3a_1$, $1b_2$, and $1b_1$ of $CH_2$ so that it becomes difficult to assign them as either ligand or metal. They are probably closely related to the frontier orbitals of $(CO)_3Ni$ and $CH_2$.

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## Concluding Remarks

We have reported the first ab initio theoretical study of a "realistic" transition-metal–carbene complex, $(CO)_3NiCH_2$. Predictions of its geometrical characteristics were reinforced by a "benchmark" optimization of the $Ni(CO)_4$ complex which was experimentally determined. The findings are for the most part consistent with geometrical and electronic expectations for this important class of organometallic species. This work suggests a variety of further studies to follow, for example, directly comparing the prototype chromium and iron carbenes (2) and (3) or replacing one carbene hydrogen with an OR or $NR_2$ ligand of the type found in Fischer carbenes. From a theoretical perspective it will also be important to directly assess the importance of correlation effects on predicted transition-metal carbene properties. Needless to say, the experimental determination of the structure and the photoelectron spectra of $(CO)_3NiCH_2$ or related prototype carbenes would be of great help in further confirming the reliability of the theoretical techniques used here.

**Acknowledgment.** We thank Professor J. Demuynck, Professor A. Veillard, and Professor M. Hall for helpful discussions. This work was supported in part by the Division of Basic Energy Sciences of the U.S. Department of Energy (Contract W-7405-ENG-48) and the National Science Foundation (Grant CHE-7721305).

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# Novel Method for Angle Determinations by EXAFS via a New Multiple-Scattering Formalism

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**Abstract:** A new EXAFS formulation which takes into account the effect of multiple scattering has been developed. Theoretical scattering amplitude and phase functions have been calculated for various scattering angles. Combining the new multiple-scattering formalism and the new theoretical functions enables the unraveling of the "focusing" effect as well as assessment of the relative importance of various multiple-scattering pathways as the scattering angle varies. On this basis, a novel method for interatomic angle determinations by EXAFS is devised and applied to a few known systems to illustrate the usefulness and accuracy of the technique. The accuracy for angle determination is better than 6% for low $Z$ ($Z \leq 10$) and 3% for high $Z$ scatterers. In most cases, it amounts to an accuracy of better than ca. 5°, which is comparable to the scattered range of crystallographically independent bond angles often observed in diffraction studies. The method requires no single-crystal measurements and is applicable to wide varieties of samples (polycrystalline or amorphous solids, liquids and solutions, gases, surfaces, polymers, etc.). This work also provides the first evidence that multiple-scattering processes can be important in determining the EXAFS of distant shells, especially at large bond angles.

The phenomenon of extended X-ray absorption fine structure (EXAFS) refers to the oscillatory modulation of the X-ray absorption coefficient as a function of X-ray photon energy beyond the absorption edge. The existence of such an extended fine structure has been known for a long time,[1] however, it is not until recently that the short-range single-electron single-scattering theory was formulated, particularly through the work of Sayers, Stern, and Lytle,[2] which led to the recognition of its structural content. For the past few years, the availability of synchrotron radiation[3] has made EXAFS spectroscopy a practical structural tool. It is particularly useful for complex or unstable chemical or biological systems where conventional diffraction methods are not applicable and/or single crystals are not available.

There are two advantageous characteristics of EXAFS spectroscopy which make it a powerful structural technique. First, being sensitive to short-range order in atomic arrangements rather than long-range crystalline order, it can focus on the *local* environment of *specific* X-ray absorbing atoms, one at a time. This allows accurate structural determination of the active site of a complex system. Second, since EXAFS signal attenuates rapidly beyond first and second coordination shells, it greatly simplifies the interpretation of the data.[4]

The major weakness of EXAFS spectroscopy is that it does not provide full stereochemical details. It gives only local structures in terms of radial distributions (distances) about the absorbing atoms. No *direct* method of determining angular information is hitherto available, except, perhaps, for elaborate measurements on single crystals by utilizing polarized X-rays.[5] In principle, though, one can argue that bond angles can be calculated if enough interatomic distances are known from EXAFS measurements of different absorbers within the same molecule. However, this indirect angle determination method is often not feasible, since not all the atoms involved are convenient X-ray absorbers (viz. the energies of their absorption edges may not be easily accessible). Furthermore, the very same advantageous characteristics of EXAFS (short range, single scattering) are also its serious limitations: distance determinations can be made out to only ca. 4 Å. The situation, however, changes dramatically when atoms (including the X-ray absorbing atom and its neighbors) are arranged in a linear or nearly collinear fashion. In such cases, EXAFS con-

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