for this bond. A (p–d)π bond order of 0.4 has been deduced from experimental bond lengths.[2] (2) The small value of the Si–O bond length is rather a consequence of its ionic character which is considerably higher than that estimated from electronegativity differences.

These conclusions should be qualitatively correct, even if we concede some arbitrariness of the Mulliken population analysis in distributing the electronic charges among the atoms and some dependence on the basis set. A similar result has been obtained previously for Si–C bonds[18] where the net charges for Si and C are about +1.0 and –0.6 au. We may assume that considerably larger ionic characters as estimated from electronegativity differences can also explain the "failure" of the Schomaker–Stevenson rule for other Si–X bonds, as demonstrated in Figure 1.

It is more difficult to correlate the increase in the bond angles upon CH_3/SiH_3 substitution in the ether-type molecules with the electronic structure. Intuitively we expect increased steric interactions due to the Si–O bond shortening. This intuition has been formulated in the "one angle nonbonded radii" concept. In disiloxane, electronic repulsions between the strongly positive silicon atoms will cause a further increase of the SiOSi angle. Such electrostatic interactions may also explain why no increase of the oxygen bond angle is observed for the peroxide, where the O···Si interaction is attractive.

Acknowledgment. This work has been supported by a grant from the Robert A. Welch Foundation. H.O. would like to express his appreciation to the North Atlantic Treaty Organization for a travel grant which has made this cooperative research possible. We thank Floyd R. Cordell for assistance with some of the calculations. Furthermore, we are grateful to the reviewers whose suggestions helped to make this paper easier to understand.

Low-Temperature Infrared Study of d^0 Carbonyl Complexes

John A. Marsella, Calvin J. Curtis, John E. Bercaw,* and Kenneth G. Caulton*

Contribution No. 3547 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47405, and No. 6211 from the Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125. *Received May 7, 1980*

Abstract: Low-temperature (–70 °C) infrared measurements have established that the carbonyl stretching frequencies of $(C_5Me_5)_2Zr(H)_2CO$ and $(C_5Me_5)_2Hf(H)_2CO$ are 2044 and 2036 cm^{-1}, respectively. The perdeuteriated complex $(C_5(CD_3)_5)_2ZrD_2CO$ exhibits a CO stretch at 2044 cm^{-1}. The unanticipated reduction of this frequency upon coordination to a d^0 metal center is rationalized in terms of back-bonding from a filled MH_2 bonding orbital of appropriate symmetry. $(C_5H_5)_2ZrCl_2$ is not carbonylated under 500 psi CO, a characteristic which is attributed to competitive π-donation by the chloro ligands. The significance of these results is discussed in relation to the hydrogenation of bound CO which ensues when $(C_5Me_5)_2M(H)_2CO$ (M = Zr, Hf) are warmed above –50 and –10 °C, respectively.

Introduction

The quest for stoichiometric or catalytic reduction of carbon monoxide by H_2 is currently proceeding in a variety of directions. One successful proposal[1] holds that transfer of a hydride ligand to coordinated CO will be favored if that hydride ligand is particularly electron rich; this characteristic has been claimed for hydrides of zirconium on the basis of both ^{1}H NMR[1] and reactivity criteria.[2] An extension of this strategy suggests that the opposite polarization of the "donor" (MH$^{\delta-}$) and the "acceptor" (MC$^{\delta+}$O) should be maximized. Thus, carbonyl complexes with minimal back-bonding to CO are appealing substrates for (intra- or intermolecular) hydrogen transfer.[3] This might be achieved in carbonyl complexes of metals in high oxidation states or those with a limited number of d electrons.

In the course of studying the homogeneous reduction of CO with $Cp^*{}_2ZrH_2$ (**1**) ($Cp^* = \eta^5\text{-}C_5(CH_3)_5$), Bercaw et al. observed the transient intermediate $Cp^*{}_2ZrH_2(CO)$ (**2**) by low-temperature NMR.[1a] In addition to the obvious mechanistic implications, the observance of this adduct is of considerable theoretical interest, since zirconium in **2** is in the +4 oxidation state and hence formally d^0. This formal absence of d electrons indicates that conventional d $\rightarrow$ π^* back-bonding from the metal to carbon monoxide cannot be operative and that the adduct should possess only simple Lewis acid–base bonding, as is the case for $BH_3{\cdot}CO$ (ν(CO) = 2165 cm^{-1} compared to 2143 cm^{-1} for gaseous CO). In light of these considerations, we have measured the low-temperature infrared spectra of $Cp^*{}_2ZrH_2(CO)$ and $Cp^*{}_2HfH_2(CO)$, another d^0 carbonyl which subsequently undergoes CO reduction.[4] These represent the first reported infrared data for d^0 carbonyl complexes.[5]

Experimental Section

Syntheses. $Cp^*{}_2ZrH_2$ was prepared as described earlier.[1b] $(Cp^*\text{-}d_{15})_2ZrD_2$ was obtained by treatment of 2 mmol of $Cp^*{}_2ZrH_2$ with five 82-mmol portions of D_2 at 72 °C over a period of 40 h.[6] A greater than 95% D incorporation was confirmed by ^{1}H and ^{2}H NMR spectrometries. $Cp^*{}_2HfH_2$ was obtained via treatment of $Cp^*{}_2HfCl_2$ with *n*-BuLi under H_2 by a procedure to be published.[4]

Spectra. A mixture of hexanes was dried over NaK alloy and vacuum distilled. IR spectra were obtained with a Perkin-Elmer 283 spectrometer. Gaseous CO was used for calibration above 2000 cm^{-1} and polystyrene for calibration below 2000 cm^{-1}.

In a typical experiment, 25 mg of the dihydride was dissolved in 1 mL of hexanes and the solution placed in a low-temperature IR cell of local design.[7] The cell is vacuum-jacketed and employs indium wire to achieve a vacuum-tight seal of the cell windows at variable temperatures. Flow-through access to the cell contents is available at all temperatures via two stainless-steel tubes which pass through the coolant well. These tubes are closed with rubber septa. The brass body of the spectral cell incorporates a chamber of 1-cm^3 volume to facilitate mixing. The solution of the dihydride was placed in this cell under N_2 in a glovebox. The cell was then cooled to –78 °C (–35 °C in the case of $Cp^*{}_2HfH_2$), and

---

* Address correspondence to K.G.C. at Indiana University or J.E.B. at the California Institute of Technology.

(1) (a) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716. (b) *Ibid.* **1976**, *98*, 6733.

(2) Labinger, J. A.; Komadina, K. *J. Organomet. Chem.* **1978**, *155*, C25.

(3) Labinger, J. A.; Wong, K. S.; Scheidt, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 3254.

(4) Fryzuk, M. D.; Seidler, P. F.; Bercaw, J. E., unpublished results.

(5) One other reported complex may also fit this description: Demersman, B.; Pankowski, M.; Bouquet, G.; Bigorgne, M. *J. Organomet. Chem.* **1976**, *117*, C10.

(6) Bercaw, J. E. *Adv. Chem. Ser.* **1978**, *No. 167*, 136.

(7) Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 1840.

0002-7863/80/1502-7244$01.00/0

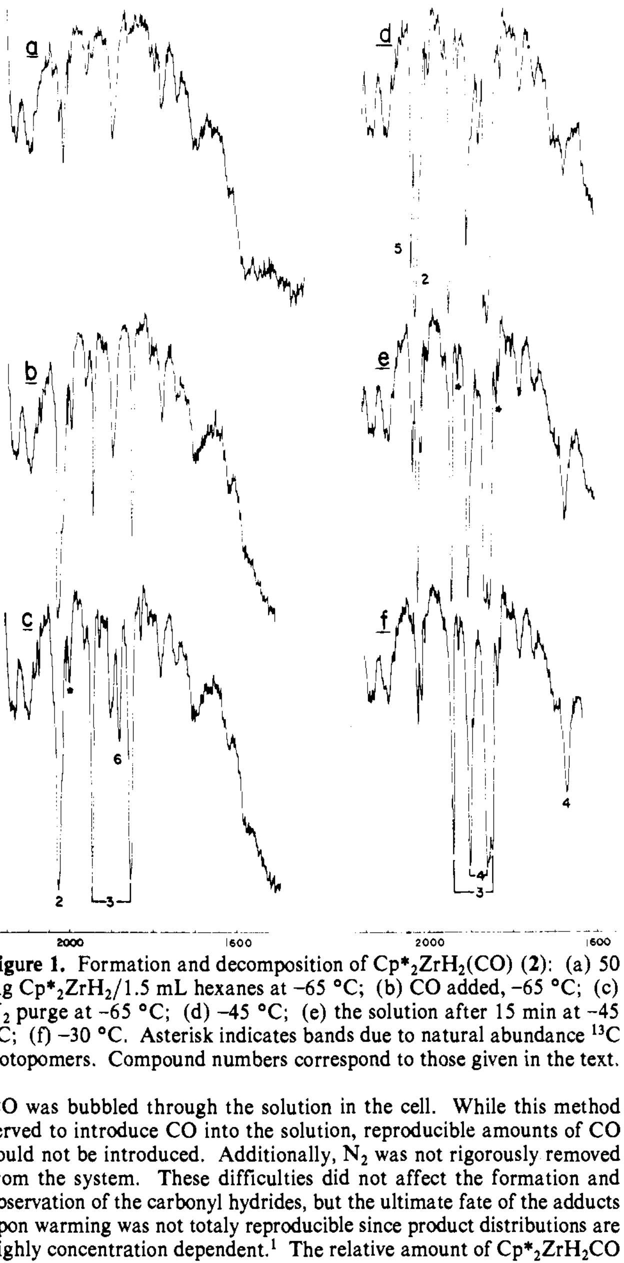


Figure 1. Formation and decomposition of $Cp^*_2ZrH_2(CO)$ (**2**): (a) 50 mg $Cp^*_2ZrH_2$/1.5 mL hexanes at -65 °C; (b) CO added, -65 °C; (c) N_2 purge at -65 °C; (d) -45 °C; (e) the solution after 15 min at -45 °C; (f) -30 °C. Asterisk indicates bands due to natural abundance ^{13}C isotopomers. Compound numbers correspond to those given in the text.

CO was bubbled through the solution in the cell. While this method served to introduce CO into the solution, reproducible amounts of CO could not be introduced. Additionally, N_2 was not rigorously removed from the system. These difficulties did not affect the formation and observation of the carbonyl hydrides, but the ultimate fate of the adducts upon warming was not totaly reproducible since product distributions are highly concentration dependent.[1] The relative amount of $Cp^*_2ZrH_2CO$ and $Cp^*_2Zr(CO)_2$ evident immediately (~5 min) after carbonylation at -78 °C is the main feature which was irreproducible. It was established that this apparent partitioning of $Cp^*_2ZrH_2$ toward two primary carbonylation products (hydrogenation of bound CO does not occur at -78 °C) was not caused by cell heating or photolysis by the infrared beam. These observations suggest that locally high CO concentrations attendant on filling the cell with gas can produce $Cp^*_2Zr(CO)_2$ (and H_2?) directly from $Cp^*_2ZrH_2$.[8]

Results and Discussion

Figure 1 shows a series of spectra obtained for the carbonylation of $Cp^*_2ZrH_2$ (**1**). The very strong band observed at 2044 cm^{-1} in the -65 °C spectrum (Figure 1b) is assigned as the CO stretch of the adduct $Cp^*_2ZrH_2(CO)$[9] (**2**). This assignment is confirmed by the ^{13}C isotopomer peak at 1999 cm^{-1}. The two sharp bands at 1950 and 1860 cm^{-1} were observed to form to a lesser extent in experiments where less CO was supplied; the relative intensity of these two bands was observed to be constant in a variety of experiments, indicating that they are due to a single species. This species is $Cp^*_2Zr(CO)_2$[1b] (**3**). Absorptions due to $Cp^*_2Zr(^{13}CO)(^{12}CO)$ in natural abundance are observed in more concentrated solutions at 1929 and 1830 cm^{-1} and serve to confirm our assignment. As the solution is allowed to warm, numerous other bands appear as the band at 2044 cm^{-1} decreases in intensity (Figure 1c–f). At -30 °C (Figure 1f), **2** has almost disappeared and strong bands at 1910, 1869, and 1671 cm^{-1} indicate the presence of $(Cp^*_2ZrCO)_2N_2$[10] (**4**). During the course of the warm-up, additional bands are evident at 2067 and 1883 cm^{-1}. The first of these bands is consistent with the highest energy terminal ν(N-N) of $(Cp^*_2ZrN_2)_2N_2$[11] (**5**); some of this compound remains visible in Figure 1e, where the 1883-cm^{-1} band is absent. In another warm-up experiment, the band at 1883 cm^{-1} formed under conditions where little or no $Cp^*_2ZrH_2(CO)$ was present. This permitted the observation that the 1883-cm^{-1} band was accompanied by another at 2024 cm^{-1}, an apparent terminal N≡N stretch. These observations, along with the position of the 1883-cm^{-1} carbonyl band (between those of **4**), are consistent with the mixed dimer $(Cp^*_2ZrCO)N{\equiv}N(Cp^*_2ZrN_2)$, **6**. As the solution was warmed, it took on a very dark violet color, consistent with that of the dimeric dinitrogen complexes.[10,11] The formation of these various Zr(II) compounds is diagnostic of CO reduction by hydrogen transfer from $Cp^*_2ZrH_2$. They represent the products of scavenging of the emerging $Cp^*_2Zr(II)$ fragment by available ligands, and their yield is thus dependent upon local concentrations of CO and N_2. The hydrogenation products themselves, $Cp^*_2ZrH(OCH_3)$ and *cis*- and *trans*-$(Cp^*_2ZrH)_2(OCHCHO)$, have no characteristic bands in the infrared region we have examined.

Carbonylation of $(Cp^*\text{-}d_{15})_2ZrD_2$ at -70 °C yielded $(Cp^*\text{-}d_{15})_2ZrD_2(CO)$ which also exhibits ν(CO) at 2044 cm^{-1}. Thus within the accuracy of these experiments (±2 cm^{-1}), we are unable to observe the magnitude of the interaction force constant for vibrational coupling of CO to M-H. It is worth noting that no vibrational coupling of CO to a cis hydride was observed for $HIrCl_2CO(PPh_3)_2$[12] even when the trans hydride ligand in $H_2IrClCO(PPh_3)_2$ is strongly coupled. In this instance, the pure M-H and CO vibrations are separated by only about 180 cm^{-1}, cf. ca. 490 cm^{-1} for $Cp^*_2ZrH_2(CO)$.

With $Cp^*_2HfH_2$, an adduct with a strong band at 2036 cm^{-1} was observed at -35 °C. Formation of $Cp^*_2Hf(CO)_2$ was negligible at this temperature. No new bands appeared as the solution was warmed to -10 °C. At -5 °C, bands assignable to $Cp^*_2Hf(CO)_2$ appeared at 1941 and 1850 cm^{-1}. As the solution warmed further, these bands increased in intensity at the expense of the band at 2036 cm^{-1}. No other bands were observed in the region 1500–2100 cm^{-1}. In neither the zirconium nor the hafnium cases were any bands assignable to metal–hydrogen stretches observed. These bands, which are broad in Nujol mulls at 25 °C, would occur from 1450 to 1600 cm^{-1},[1a] a region in which solvent absorption becomes significant. No bands assignable to metal formyl intermediates were observed in this region.

The observation of ν(CO) for $Cp^*_2ZrH_2(CO)$ and $Cp^*_2HfH_2(CO)$ near 2040 cm^{-1} is to be compared to the value found for free carbon monoxide (2143 cm^{-1})[13a] and $BH_3{\cdot}CO$ (2165 cm^{-1}).[13a] The monocarbonyls of a wide variety of transition-metal difluorides all show CO frequencies well above 2143 cm^{-1}.[13b,c] While these d^0 carbonyls exhibit CO stretching frequencies which are markedly higher than those of the d^2 species $(C_5H_5)_2Zr(CO)_2$[14]

---

[8] Recent low-temperature ^1H NMR studies under more carefully controlled CO concentrations support these suppositions. At higher CO pressures (>500 torr) formation of *trans*-$(Cp^*_2ZrH)_2(OCHCHO)$ is suppressed and $Cp^*_2Zr(CO)_2$ (and presumably H_2) are produced in a first-order process at -40 °C. At lower CO pressures (<200 torr) the rate of decomposition of $Cp^*_2ZrH_2(CO)$ is markedly increased as is the relative yield of *trans*-$(Cp^*_2ZrH)_2(OCHCHO)$. Curtis, Calvin J.; Bercaw, J. E. experiments in progress.

[9] This frequency is unreasonably high for alternative structures such as a formyl complex or the hypothetical unsaturated species Cp^*_2ZrCO.

[10] Manriquez, J. M.; Sanner, R. D.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 3042.

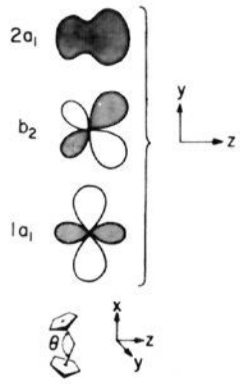
[11] Manriquez, J. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 6229.

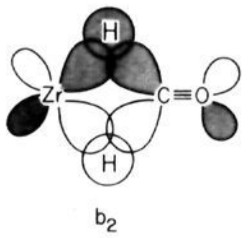
[12] Vaska, L. *J. Am. Chem. Soc.* **1966**, *88*, 4100.

[13] (a) Nakamoto, Kazuo, Ed. "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed.; Wiley-Interscience: New York, 1970; p 78. (b) Van Leirsburg, D. A.; DeKock, C. W. *J. Phys. Chem.* **1974**, *78*, 134. (c) Hauge, R. H.; Grandsen, S. E.; Margrave, J. L. *J. Chem. Soc., Dalton Trans.* **1979**, 745.

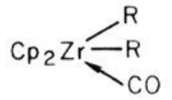
[14] Fachinetti, G.; Fochi, G.; Floriani, C. *Chem. Soc., Chem Commun.* **1976**, 230.

(1976, 1887 cm^{-1}), $(C_5Me_5)_2Zr(CO)_2$, and $(C_5H_5)_2MoCO$ (1931 cm^{-1}) (all in hexane or heptane) the unanticipated 100-cm^{-1} *reduction* of the CO frequency in **3** is in fact the feature which requires explanation. This is particularly true since comparable stretching frequencies are found among other carbonyl complexes possessing an abundance of d electrons: $NiI_2CO(PMe_3)_2$[15] at 2015 cm^{-1}, $Pt(THF)COCl_2$[16] at 2090 cm^{-1}, and $AuCOCl$[16] at 2158 cm^{-1}. A reasonable explanation for this decrease in stretching frequency is that electron density from the filled b_2 metal hydride bonding orbital[17] is back-donated to the in-plane π^* CO orbital of b_2 symmetry (structure **I**,[18] Cp = C_5H_5). This type of back-bonding was first postulated by Brintzinger[19] in order to explain the apparent preference for central coordination of CO in $Cp^*_2ZrH_2(CO)$ while $Cp_2Zr(C_6H_5)_2$ and $Cp_2Zr(CH_3)_2$ apparently form adducts with CO in the lateral position (II) before subsequent R-group migration.[20] Lauher and Hoffmann[17] earlier recognized that overlap of this type is also possible in the lateral isomer II. The extent of the back-bonding in $Cp^*_2ZrH_2(CO)$ and $Cp^*_2HfH_2(CO)$ can be gauged by comparison with two recently reported Ti(III) (d^1) carbonyls: $Cp_2Ti(C_6F_5)CO$ (2060 cm^{-1}) and $Cp^*_2TiCl(CO)$ (2000 cm^{-1}).[21]





I



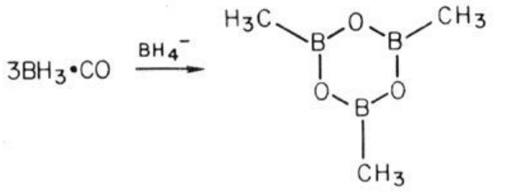
II

The magnitude of the coupling constant between the carbonyl carbon and the hydride hydrogens, $J_{^{13}C-H}$ = 25 and 23.5 Hz[4] for $Cp^*_2ZrH_2(^{13}CO)$ and $Cp^*_2HfH_2(^{13}CO)$, respectively, appears to further support overlap of the filled, in-plane b_2 metal hydride orbital with the π^* CO orbital. A purely σ adduct would be expected to exhibit a $J_{^{13}C-H}$ of only 2–3 Hz, considering the value of the J_{HH} (10 Hz)[22] observed for the structurally similar compound Cp_2TaH_3 and the relative nuclear magnetic moments ($\mu_{^1H}/\mu_{^{13}C}$ = 3.98). The fact that the observed coupling constant is an order of magnitude larger may be indicative of additional bonding proposed above, which could be likened to hyperconjugation.[23,24]

In an attempt to obtain a ν(CO) value indicative of a simple Lewis acid–base zirconium–CO adduct, we treated a CH_2Cl_2 solution of Cp_2ZrCl_2 with 500 psi of CO in a reaction vessel equipped with a high-pressure IR cell. The spectrum of the resulting solution at 500-psi pressure showed only the presence of dissolved CO. No band assignable to $Cp_2ZrCl_2(CO)$ was observed. This is in accord with π donation from the chloride ligand to zirconium,[20,25,26] reducing the availability of the empty $2a_1$ metal orbital for Zr–C σ-bond formation. Alternatively, the lack of adduct formation may be ascribed to the inability of Zr–Cl bonds to engage in back donation (I).

Recent work[1,27] has revealed the considerable complexity of the reactions of $Cp^*_2ZrH_2CO$ upon warming above −78 °C. The initial proposal of a $Cp^*_2ZrH(\eta^2\text{-}CHO)$ intermediate is no longer compelling or even attractive.[27] In view of the demonstrated ability of $Cp^*_2ZrH_2$ to add Zr–H across the CO bond of a variety of metal carbonyls,[28] it may be that bimolecular hydrogen transfer from this "decarbonylated" hydride (eq 1) to $Cp^*_2ZrH_2CO$ is essential to the successful CO reduction which ensues on warming $Cp^*_2ZrH_2CO$. While equilibrium 1 lies to the left under 1 atm CO at −78 °C, the effect of warming may be as much to shift this equilibrium to the right as it is to increase reaction rate.[8] Bimolecular CO hydrogenation becomes possible only when both $Cp^*_2ZrH_2$ and $Cp^*_2ZrH_2CO$ achieve significant concentrations. Viewed in this way, the 2044-cm^{-1} carbonyl stretching frequency of $Cp^*_2ZrH_2CO$ makes this an obvious target for hydride transfer. The efficacy of this mechanism is strongly reminiscent of the reduction of CO by BH_3. While BH_3CO is itself stable, BH_4^- *catalyzes* its reduction according to eq 2.[29] The parallel utilization of a pure (BH_3) or nearly pure ($Cp^*_2ZrH_2$) σ-Lewis acid and an electron-rich hydride (BH_4^- and $Cp^*_2ZrH_2$) thus forms the basis of a successful strategy for stoichiometric reduction of CO among both representative and transition elements. The peculiar feature of the $Cp^*_2ZrH_2$ system is that the same molecule will bind (activate) CO and also serve as a hydrogen source, though not perhaps in an intramolecular fashion.

$$Cp^*_2ZrH_2CO \xrightleftharpoons[>-78\ ^\circ C]{} Cp^*_2ZrH_2 + CO \qquad (1)$$



(2)

Acknowledgment. The design and construction of the infrared cell would have been impossible without the craftsmanship of Dick Martin and John Dorsett. This work was supported by the National Science Foundation (Grants CHE 77-10059 (K.G.C.) and CHE-50006 (J.E.B)).

---

(15) Saint-Joly, C.; Dartiguenave, M.; Dartiguenave, Y. *Adv. Chem. Ser.* **1979**, *No. 173*, 152.

(16) Dell'Amico, D. B.; Calderazzo, F.; Dell'Amico, G. *Gazz. Chim. Ital.* **1977**, *107*, 101.

(17) Lauher, J. W.; Hoffman, R. *J. Am Chem. Soc.* **1976**, *98*, 1729.

(18) This assumes central binding of CO based upon the NMR results of the Bercaw group. Our infrared data are not structurally diagnostic of this point.

(19) Brintzinger, H. H. *J. Organomet. Chem.* **1979**, *171*, 337.

(20) Erker, G.; Rosenfeld, F. *Angew. Chem.* **1978**, *90*, 640; *J. Organomet. Chem.* **1980**, *188*, C1.

(21) DeBoer, E. J. M.; Ten Cate, L. C.; Staring, A. G. J.; Teuben, J. H. *J. Organomet. Chem.* **1979**, *181*, 61.

(22) Green, M. L. H.; McCleverty, J. A.; Pratt, L.; Wilkinson, G. *J. Chem. Soc. A* **1961**, 4854.

(23) Pauling, Linus, Ed. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 308.

(24) On the other hand, a geminal ^{13}C–H coupling constant of 20 Hz has been reported recently for the binuclear tantalum compound $(\eta^5\text{-}C_5Me_4Et)Cl_2\mathit{H}Ta(\mu\text{-}\mathit{C}HO)TaCl_2(\eta^5\text{-}C_5Me_4Et)$: Belmonte, P.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 2858.

(25) Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009.

(26) Marsella, J. A.; Moloy, K. G.; Caulton, K. G. *J. Organomet. Chem.*, in press.

(27) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121.

(28) Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 218.

(29) Rathke, M. W.; Brown, H. C. *J. Am. Chem. Soc.* **1966**, *88*, 2606.