Organometallics 1982, *1*, 699–703

An X-ray Photoelectron Spectroscopic Study of the Bonding in (Alkylidyne)tricobalt Nonacarbonyl Complexes and Related Compounds

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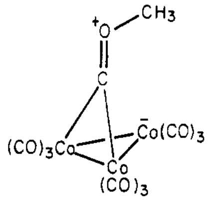
Received September 15, 1981

The core electron binding energy of the methylidyne carbon atom in $RC[Co(CO)_3]_3$ compounds is a function of the electronegativity of the R group; the trend of binding energy with R group is similar to that for the methyl carbon atom in the corresponding RCH_3 compounds. The core binding energies of the $[Co(CO)_3]_3$ cluster generally change similarly, but to a smaller extent, with changing R group. However, for R = OCH_3 and R = $N(CH_3)_2$, the core binding energies of the $[Co(CO)_3]_3$ cluster are significantly lower than expected. These data, and a combination of UPS and XPS data for the chloro and bromo compounds, indicate that groups such as OCH_3, $N(CH_3)_2$, Cl, and Br act as π donors toward the $C[Co(CO)_3]_3$ system. Binding energy data indicate that the CH groups of $HC[Co(CO)_3]_3$ and $(HC)_2[Co(CO)_3]_2$ are negatively charged, with the CH group of $HC[Co(CO)_3]_3$ more negative than those of $(HC)_2[Co(CO)_3]_2$. The significantly lower binding energies of $[Co(CO)_3]_4$ reflect the fact that three of the carbonyl groups in this compound are bridging.

The nature of the bonding in the (alkylidyne)tricobalt nonacarbonyl complexes, $RC[Co(CO)_3]_3$, is a topic which has intrigued chemists ever since the first characterization of these compounds.[2] According to polyhedral cluster theory,[3] the $Co(CO)_3$ group is analogous to the CH group; therefore the parent complex $HC[Co(CO)_3]_3$ can be looked upon as an analogue of tetrahedrane. The complexes may also be considered as analogues of CR groups chemisorbed on a metal surface. Clearly the nature of the interaction of the CR groups with the $Co_3(CO)_9$ cluster is of interest. In this study we have used gas-phase X-ray photoelectron spectroscopy (XPS) to probe the valence-electron density on the various atoms in this family of complexes and, for comparison, in compounds which are structurally and electronically related. For each compound we have obtained spectra in the Co $2p_{3/2}$, O 1s, and C 1s regions. Each C 1s spectrum shows a strong peak near 293 eV due to the CO groups and a band near 290 eV due to the CR groups. As an example, the C 1s spectrum of the parent compound, $HC[Co(CO)_3]_3$, is shown in Figure 1.

The $RC[Co(CO)_3]_3$ Compounds. The binding energy data for the $RC[Co(CO)_3]_3$ compounds are presented in Table I. The binding energy of the methylidyne carbon atom appears to be a straightforward function of the electronegativity of the attached R group. Indeed the trend in binding energies of the methylidyne carbon atom is very similar to that of the methyl carbon atom in the corresponding RCH_3 compounds.[4] To emphasize this correlation and the normalcy of the methylidyne binding energies, we have plotted these binding energies against one another in Figure 2.

The binding energies of the cobalt atoms and the carbon and oxygen atoms of the carbonyl groups are relatively insensitive to changes in the R group. However, slight effects can be seen as the electronegativity of R is changed. Thus, in each set the binding energy is low when R is the relatively electropositive $SiEt_3$ group and is high when R is the relatively electronegative chloro group. The remarkable feature of the data is that the cobalt and carbonyl binding energies of the methoxy and dimethylamido compounds are much lower than one might expect on the basis of the high electronegativities of these groups. The lowest binding energies in each of the three sets (cobalt, carbonyl oxygen, and carbonyl carbon binding energies) are those for the compounds with R = $SiEt_3$, OCH_3, and $N(CH_3)_2$. The relatively low net electron withdrawal by the methoxy and dimethylamido groups is probably related to the fact that these groups have readily available nonbonding π-electron density and are very good π-donor groups.[5] We believe that the data indicate strong π-donor interaction of the methoxy and dimethylamido groups with the $CCo_3(CO)_9$ cluster, of the type implied by the following valence-bond resonance structure.



This type of delocalized π bonding between the R group and the $CCo_3(CO)_9$ cluster has been suggested in previous studies. Thus Miller and Brill[6] have observed that ^{59}Co NQR coupling constants correlate with the Hammett σ_R parameters for the R group but show no correlation with the corresponding σ_I parameters. Chesky and Hall[7] have found that both UPS spectra and MO calculations are consistent with a π-bonding system in the cluster that can act either as a donor or an acceptor. They propose that the methylidyne carbon forms a bond to the metal triangle with an sp hybrid orbital and that the two remaining p orbitals form multicentered π bonds to the Co_3 system.

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(5) For example, the Hammett σ_R values for OCH_3 and NH_2 are much more negative than the values for Cl and Br. See: Shorter, J. "Correlation Analysis in Organic Chemistry"; Clarendon Press: Oxford, 1973; p 18.

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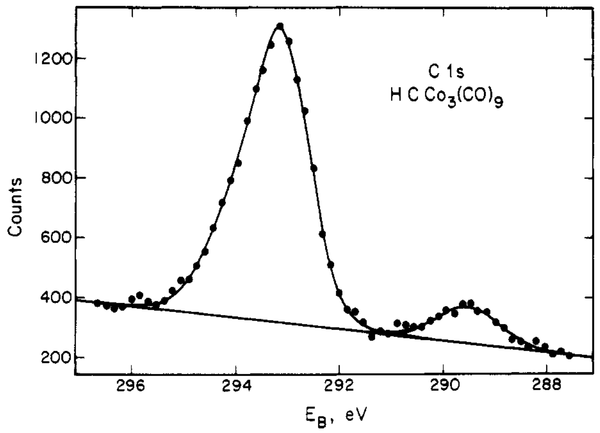

Figure 1. Carbon 1s spectrum of $HC[Co(CO)_3]_3$ vapor.

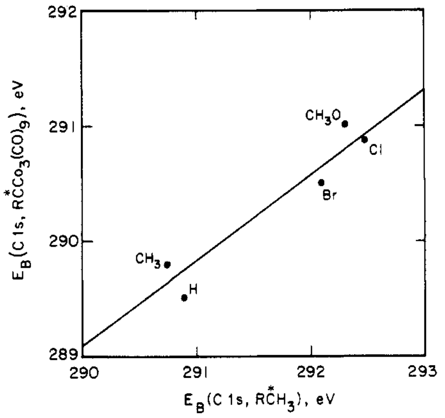

Figure 2. Plot of carbon 1s binding energy for the methylidyne carbon atom of $RC[Co(CO)_3]_3$ vs. the carbon 1s binding energy of the methyl group of RCH_3.

Analogous Compounds. Because of the formal electronic analogy of the CH group and the $Co(CO)_3$ group, we have studied other tetrahedral cluster compounds containing these groups, i.e., $[Co(CO)_3]_4$, $(HC)_2[Co(CO)_3]_2$, and derivatives of these compounds. The binding energy data are given in Table II. First let us compare the three acetylene complexes, or C_2Co_2 cluster compounds. Substitution with the relatively electron-donating Me_3Si and Me_3C groups, as expected, causes all the binding energies to decrease significantly. The differences between the compound with two Me_3Si groups and that with one Me_3Si and one Me_3C group are only about twice the uncertainties in the data, and we have no explanation for these small differences.

On going from $HC[Co(CO)_3]_3$ to $(HC)_2[Co(CO)_3]_2$, the cobalt and carbonyl carbon binding energies decrease slightly, and the oxygen binding energy is essentially constant. We conclude that, in these two compounds, the electron densities on the $Co(CO)_3$ groups are similar, with slightly more electron density on the $Co(CO)_3$ groups of $(HC)_2[Co(CO)_3]_2$.

There is a marked decrease in the C 1s binding energy of the CH carbon atom on going from $(HC)_2[Co(CO)_3]_2$ to $HC[Co(CO)_3]_3$. This result suggests that the CH group of $HC[Co(CO)_3]_3$ is more negatively charged than the CH groups of $(HC)_2[Co(CO)_3]_2$. Indeed this conclusion is consistent with the other binding energies, which suggest that the $Co(CO)_3$ groups in $(HC)_2[Co(CO)_3]_2$ have slightly more electron density than those in $HC[Co(CO)_3]_3$. However, in molecules like these it is dangerous to interpret binding energy shifts simply in terms of changes in atomic charge. A complete analysis should also take ac-

Table I. Core Binding Energies (eV) and Line Widths (eV) of (Alkylidyne)tricobalt Nonacarbonyl Clusters, $RC[Co(CO)_3]_3$ [a]

R in $RC[Co(CO)_3]_3$	Co $2p_{3/2}$		O 1s		C 1s					
	E_B	fwhm	E_B	fwhm	E_B (RC*)	fwhm	E_B (R)	fwhm	E_B (CO)	fwhm
Et_3Si	786.18 (5)	1.42 (16)	539.48 (4)	1.60 (11)	...	...	289.95 (7)[b]	1.74 (24)	293.09 (6)[b]	1.27 (21)
H	786.38 (5)	1.30 (11)	539.63 (5)	1.58 (10)	289.50 (8)	1.38 (20)			293.32 (3)	1.48 (6)
CH_3	786.26 (4)	1.34 (10)	539.56 (4)	1.56 (11)	289.79 (12)[c]	0.96 (24)	290.74 (12)[c]	0.96 (24)	293.32 (4)[c]	1.46 (9)
Br	786.33 (4)	1.36 (8)	539.66 (5)	1.50 (10)	290.5 (2)	1.3 (6)			293.28 (4)	1.34 (11)
Cl	786.38 (4)	1.38 (9)	539.67 (6)	1.56 (15)	290.87 (10)	1.20 (21)			293.34 (5)	1.52 (10)
$(CH_3)_2N$	786.21 (8)	1.32 (26)	539.28 (10)	1.99 (49)	...	...	...	...	293.23 (14)[d]	1.97 (45)
CH_3O	786.11 (4)	1.41 (11)	539.47 (4)[e]	1.68 (10)	291.0 (2)[c]	1.25	292.0 (2)[c]	1.25	293.08 (4)[c]	1.57 (7)

[a] The uncertainty in the last digit (usually estimated as twice the standard deviation determined by the least-squares fit) is indicated parenthetically. [b] Deconvoluted assuming E_B = 289.2 eV for the methylidyne carbon and an intensity ratio of 6:1. For the unresolved peak, E_B = 289.87 eV. [c] Deconvoluted assuming an intensity ratio of 9:1:1 for the three kinds of carbon atoms. [d] Deconvoluted assuming an average value of E_B = 291.3 eV for the $(CH_3)_2NC$ group and an intensity ratio of 3:1. For the unresolved peak, E_B = 293.12 eV. [e] Deconvoluted assuming E_B = 538.7 eV for the CH_3O oxygen and an intensity ratio of 9:1. For the unresolved peak, E_B = 539.41 eV.

Table II. Core Binding Energies of $[Co(CO)_3]_4$ and Some Related Compounds (eV)[a]

			C 1s		
compd	Co $2p_{3/2}$	O 1s	CO	CH or C*R	C^*H_3
$[Co(CO)_3]_4$	785.75 (3)	539.43[b]	293.22 (7)		
$HC[Co(CO)_3]_3$	786.38 (5)	539.63 (5)	293.32 (3)	289.50 (8)	
$(HC)_2[Co(CO)_3]_2$	786.23 (4)	539.69 (4)	293.24 (3)	290.08 (6)	
$(Me_3SiC)_2[Co(CO)_3]_2$	785.97 (4)	539.37 (5)	292.99 (8)		289.80 (5)[c]
$(Me_3CC)(Me_3SiC)[Co(CO)_3]_2$	785.92 (4)	539.23 (6)	292.74 (8)	289.3 (2)[d]	290.3 (2)[d]
$(CO)_3FeCo_3(CO)_9H$	785.86 (7)	539.19[b]	293.36 (7)		
C_2H_2				291.14[e]	

[a] The uncertainty in the last digit (generally estimated as twice the standard deviation determined by the least-squares fit) is indicated parenthetically. [b] Weighted average for the bridging and terminal carbonyl groups. The individual peaks were deconvoluted as follows. For $Co_4(CO)_{12}$, $E_B(\mathrm{br}) = 538.48$ (17), $E_B(\mathrm{t}) = 539.75$ (7) eV. For $FeCo_3(CO)_{12}H$, $E_B(\mathrm{br}) = 538.08$ (14), $E_B(\mathrm{t}) = 539.56$ (7). [c] Single peak observed for six CH_3 and two cluster carbons. [d] "Organic" C band deconvoluted into two peaks with 2:1 intensity ratio. Stronger peak corresponds to average CH_3 group, weaker to average of central *tert*-butyl and two cluster carbons. [e] Reference 4.

Table III. Calculated Charges on CH Groups Using C 1s Binding Energies and the Potential Equation

	charge on CH group	
compd	including ΔE_R term	assuming $\Delta E_R = 0$
$HC[Co(CO)_3]_3$	−0.50	−0.67
$(HC)_2[Co(CO)_3]_2$	−0.17	−0.28

count of changes in potential due to all the groups in the molecules and changes in electronic relaxation energy accompanying core emission.[8] In transition-metal carbonyl complexes, the relaxation energy term can account for a large part of the binding energy shift.[9] Presumably the $Co(CO)_3$ group is considerably more polarizable than the CH group, and therefore one would expect greater relaxation energy for a CH group bonded to three $Co(CO)_3$ groups than for one bonded to two $Co(CO)_3$ groups and a CH group. In order to obtain at least qualitative information regarding the actual charges on the CH groups in these compounds, we have analyzed the CH carbon binding energy data for acetylene (in which the CH group obviously has zero charge), $HC[Co(CO)_3]_3$, and $(HC)_2[Co(CO)_3]_2$ using the "potential equation",[8] both with and without inclusion of the relaxation energy term. Relaxation energies were estimated by a modification of the transition-state method,[10] using CNDO/2 wave functions and the equivalent cores approximation.[11] The assumptions made and details of the method of calculation are summarized in the Experimental Section, and the results are given in Table III. The relaxation energies used in the calculations are half of the values obtained by straightforward application of the transition-state method. A correction factor of about half in conjunction with CNDO charges was found in earlier work to give satisfactory correlations of binding energy data for $LMn(CO)_5$ compounds[12] and for compounds of nitrogen and phosphorus;[13] it seems likely that such corrected relaxation energies are more appropriate for this system than the uncorrected values. In spite of the uncertainties in the relaxation energies, we believe that the charges based on relaxation energies are much more reliable than those calculated on the unreasonable basis of zero relaxation energy. Taking account of the considerable uncertainties in the calculations, we conclude that the charges on the CH groups in $HC[Co(CO)_3]_3$ and $(HC)_2[Co(CO)_3]_2$ are −0.5 ± 0.2 and −0.2 ± 0.2, respectively. The result for $HC[Co(CO)_3]_3$ is consistent with recent UPS[7] and X-ray diffraction data[14] which indicate that the $Co_3(CO)_9$ cluster in this molecule is electron releasing. The fact that the $Co_3(CO)_9$ group can accept π-electron density from groups such as CH_3OC and donate electron density to CH shows that the $Co_3(CO)_9$ cluster possesses a "flexible" π system[7] and that electronic relaxation or polarization is sometimes more important than ground-state molecular properties in determining chemical reactivity.[15]

On going from $HC[Co(CO)_3]_3$ or $(HC)_2[Co(CO)_3]_2$ to $[Co(CO)_3]_4$, the cobalt binding energy decreases markedly and the carbonyl binding energies decrease slightly but significantly. We believe these changes are due to the basic structural difference between $[Co(CO)_3]_4$ and the CCo_3 and C_2Co_2 cluster compounds. In $[Co(CO)_3]_4$ three of the carbonyl groups are bridging between pairs of cobalt atoms on the edges of one face of the Co_4 tetrahedron. Bridging CO groups are known to have lower binding energies than terminal CO groups,[16] and thus the weighted average binding energy of the CO groups in $[Co(CO)_3]_4$ is lower than one would expect if all the groups were terminal. We believe that the cobalt binding energy of $[Co(CO)_3]_4$ is lower than in the unbridged CCo_3 and C_2Co_2 compounds because the average number of coordinated CO groups is 3.75 rather than 3, and consequently the relaxation energy is greater. It has been previously noted that the electron-flow contribution to relaxation energy increases with an increase in the number of bonds, or avenues for electron flow.[17,18]

It is interesting that the cobalt, oxygen, and carbon binding energies of $(CO)_3FeCo_3(CO)_9H$ (which is isoelectronic and isostructural with $[Co(CO)_3]_4$) are similar to those of $[Co(CO)_3]_4$.

Information from Valence-Shell Ionization Potentials. Evidence for increased back-bonding in $Co_4(CO)_{12}$ due to the bridging carbonyl groups can be obtained from

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a combination of UPS and XPS spectral data. The low-energy bands due to the "nonbonding" cobalt 3d orbitals observed in the UPS spectra of $HC[Co(CO)_3]_3$, $CH_3C[Co(CO)_3]_3$, $ClC[Co(CO)_3]_3$, $BrC[Co(CO)_3]_3$, $CH_3OC[Co(CO)_3]_3$, and $(HC)_2[Co(CO)_3]_2$ appear at 8.8, 8.7, 8.8, 8.9, 8.6, and 8.7 eV, respectively.[7,19–21] These values are very similar to the corresponding value for $Co_4(CO)_{12}$, viz., 8.9 eV.[21,22] However, for these data to be used to judge the relative bonding characters of the 3d orbitals, the ionization potentials for the $RC[Co(CO)_3]_3$ compounds should be corrected for the changes in relaxation energy and atomic charge on going from $Co_4(CO)_{12}$ to $RC[Co(CO)_3]_3$. This can be approximately accomplished[23] by subtracting from each ionization potential eight-tenths of the difference in the cobalt $2p_{3/2}$ binding energy $0.8[E_B(RCCo_3(CO)_9) - E_B(Co_4(CO)_{12})]$. Thus we calculate that, if all the potentials and relaxation energies were the same as those of $[Co(CO)_3]_4$, the $RC[Co(CO)_3]_3$ and $(HC)_2[Co(CO)_3]_2$ ionization potentials would be 8.3, 8.3, 8.3, 8.4, 8.3, and 8.3 eV, respectively. These values are remarkably similar and are about 0.6 eV lower than the cobalt $3d\pi$ ionization potential of $Co_4(CO)_{12}$. Clearly the cobalt 3d orbitals of the $RC[Co(CO)_3]_3$ compounds and $(HC)_2[Co(CO)_3]_2$ are very similar in character and have about 0.6 eV less π-bonding character than the corresponding orbitals in $Co_4(CO)_{12}$.

Similar calculations can be made for the valence $p\pi$ orbitals of the halogen atoms in $ClC[Co(CO)_3]_3$ and $BrC[Co(CO)_3]_3$, using the ionization potentials obtained from UPS spectra. We may reasonably assume that the lowest ionization potentials of HCl and HBr (12.8 and 11.8 eV, respectively[21,24]) correspond to strictly nonbonding halogen $p\pi$ orbitals. From the differences in the halogen core binding energies[4] between $XC[Co(CO)_3]_3$ and HX, we calculate the following values for hypothetical nonbonding $p\pi$ orbitals in the $XC[Co(CO)_3]_3$ compounds. For $ClC[Co(CO)_3]_3$

$$12.8 + 0.8(205.69 - 207.39) = 11.4 \text{ eV}$$

For $BrC[Co(CO)_3]_3$

$$11.8 + 0.8(75.64 - 77.36) = 10.4 \text{ eV}$$

The observed ionization potentials for $ClC[Co(CO)_3]_3$ and $BrC[Co(CO)_3]_3$, 12.3 and 11.6 eV, respectively,[7,19,21] are higher than the estimated nonbonding ionization potentials and thus are consistent with π-bonding between the halogen atoms and the $CCo_3(CO)_9$ clusters. Unfortunately the appropriate valence and core ionization potentials for the CH_3O oxygen atom of $CH_3OC[Co(CO)_3]_3$ and the nitrogen atom of $Me_2NC[Co(CO)_3]_3$ have not been measured. Calculations using these data would allow us to test our conclusion, based on core binding energies alone, that these systems have even stronger π interactions between the R groups and the $CCo_3(CO)_9$ clusters.

Experimental Section

The spectra were obtained in the gas phase using procedures described previously.[25] N_2 gas was run simultaneously with the compounds to obtain more accurate calibration. A computer program corrected the peak centers for drift after every few scans. We also made some improvements in the fitting program[26] to allow for vibrational broadening and the X-ray doublet. For instance, the Mg $K\alpha_2$ line was assigned half the intensity of and an energy 0.33 eV higher than the $K\alpha_1$ line.[27] The new version of the fitting program expresses each peak in a spectrum as a sum of several lines. However, all our reported binding energies are "vertical" ionization potentials, corresponding to the weighted averages of the constituent peak centers. The cluster compounds $HC[Co(CO)_3]_3$ and $(HC)_2[Co(CO)_3]_3$, and most of the related substituted derivatives, are volatile enough that we were able to obtain their spectra at room temperature. However, it was necessary to maintain $Et_3SiC[Co(CO)_3]_3$ and $[Co(CO)_3]_4$ at 40 °C and $H[Fe(CO)_3][Co(CO)_3]_3$ at 50 °C in order to obtain satisfactory spectra. All the binding energies are based on spectrometer calibrations with the free nitrogen N 1s, Ne 1s, and Ne 2s lines, except the O 1s and C 1s spectra of $(CH_3)_2NC[Co(CO)_3]_3$ where it was possible to measure the binding energies relative to the decomposition product, carbon monoxide. Some of the core binding energies have been published previously.[28] Several binding energies, not given in Tables I and II, were measured. These and the corresponding line widths are listed here. $ClC[Co(CO)_3]_3$: Cl $2p_{3/2}$ 205.69 (6) eV, 1.53 (12) eV; Cl $2p_{1/2}$ 207.29 (10) eV, 1.46 (19) eV. $BrC[Co(CO)_3]_3$: Br $3d_{5/2}$ 75.64 (10) eV, 1.80 (30) eV. $Et_3SiC[Co(CO)_3]_3$: Si $2p_{3/2}$ 105.73 (10) eV, 1.22 (28) eV. $(Me_3CC)(Me_3SiC)[Co(CO)_3]_2$: Si $2p_{3/2}$ 106.2 (2) eV, 2.1 (9) eV. $(Me_3SiC)_2[Co(CO)_3]_2$: Si $2p_{3/2}$ 106.22 (10) eV, 1.49 (26) eV.

The compounds $HC[Co(CO)_3]_3$,[29] $ClC[Co(CO)_3]_3$,[30] and $BrC[Co(CO)_3]_3$[31] were prepared according to published procedures, described previously.[28] A sample of $CH_3C[Co(CO)_3]_3$ was kindly provided by L. Stuhl. The $(HC)_2[Co(CO)_3]_2$ was prepared by the method of Greenfield et al.[32] The product melted at 12.5–13 °C (lit. mp 13 °C) and was shown to be pure by its ^1H and ^{13}C NMR spectra, using C_6D_6 solvent. The $[Co(CO)_3]_4$ was prepared by the method of Chini et al.[33] and sublimed twice. The infrared spectrum agreed with the literature.[33] The compounds $Et_3SiC[Co(CO)_3]_3$,[34] $(CH_3)_2NC[Co(CO)_3]_3$,[35] $CH_3OC[Co(CO)_3]_3$,[35] $(Me_3SiC_2SiMe_3)[Co(CO)_3]_2$,[36] and $(Me_3CC_2SiMe_3)[Co(CO)_3]_2$[37] were prepared and characterized by the referenced procedures. The $HFeCo_3(CO)_{12}$ was kindly supplied by Dr. M. Tachikawa. This compound was sublimed immediately before use; its infrared spectrum agreed with that in the literature.[38]

The change in charge of the CH carbon atom (ΔQ_C) on going from acetylene to $HC[Co(CO)_3]_3$ or $(HC)_2[Co(CO)_3]_2$ was calculated by using the equation

$$\Delta E_B = k\Delta Q_C + \Delta V - \Delta E_R$$

where ΔE_B is the change in the C 1s binding energy, k is 22.1 eV/charge,[39] ΔV is the change in potential due to the charges of

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the other atoms, and ΔE_R is the change in relaxation energy. The E_R values were calculated from the relation $E_R = 0.25[\Phi_{val}(C) - \Phi_{val}(N^+)$, where $\Phi_{val}(C)$ is the valence potential in the ground-state molecule and $\Phi_{val}(N^+)$ is the valence potential in the ion, approximated by replacing the C nucleus by the N nucleus.[12,13] CNDO/2 wave functions were used.[40] We assumed that the relative valence-electron populations of the atoms in the $Co(CO)_3$ groups were the same as calculated for $HCo(CO)_4$,[41] that $Q_C = -0.2$ in acetylene,[42] and that $(\Delta Q_H/\Delta Q_C) = 0.2$.[43] The experimental geometry of C_2H_2[44] was used, and symmetric idealized geometries for $HC[Co(CO)_3]_3$[45] and $(HC)_2[Co(CO)_3]_2$[46] were assumed. In the cobalt complexes, we assumed Co–CO and C–O bond distances of 1.8 and 1.1 Å, and a C–H bond distance equal to that in benzene. The calculated relaxation energies for C_2H_2, $HC[Co(CO)_3]_3$, and $(HC)_2[Co(CO)_3]_2$ are 7.68, 10.35, and 10.18 eV, respectively.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of The U.S. Department of Energy under Contract No. DE-AC03-76SF00098 and by the National Science Foundation (Grant CHE-816769).

Registry No. $Et_3SiC[Co(CO)_3]_3$, 64115-67-9; $HC[Co(CO)_3]_3$, 15664-75-2; $CH_3C[Co(CO)_3]_3$, 13682-04-7; $BrC[Co(CO)_3]_3$, 19439-14-6; $ClC[Co(CO)_3]_3$, 13682-02-5; $(CH_3)_2NC[Co(CO)_3]_3$, 41751-69-3; $CH_3O-C[Co(CO)_3]_3$, 41751-68-2; $[Co(CO)_3]_4$, 17786-31-1; $(HC)_2[Co(CO)_3]_2$, 12264-05-0; $(Me_3SiC)_2[Co(CO_3)]_2$, 14767-82-9; $(Me_3CC)(Me_3SiC)-[Co(CO)_3]_2$, 80926-03-0; $(CO)_3Fe(Co_3(CO)_9H$, 21750-96-9.

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Preparation of Tantalum μ-Dinitrogen Complexes from Molecular Nitrogen and Reduced Tantalum Complexes

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Received December 9, 1981

Tantalum pentachloride is reduced under argon by sodium amalgam in the presence of PMe_3 to give red paramagnetic $TaCl_3(PMe_3)_3$ in 80% yield. It decomposes readily in solution to give $[TaCl_3(PMe_3)_2]_2$. It reacts with hydrogen to give $[TaCl_3(PMe_3)_2]_2H_2$ and with ethylene to give *trans*-$Ta(C_2H_4)(PMe_3)_2Cl_3$, but it does not react with molecular nitrogen to give known $[TaCl_3(PMe_3)_2]_2(\mu\text{-}N_2)$. $Ta(C_2H_4)(PMe_3)_2Cl_3$ is reduced by sodium amalgam in the presence of PMe_3 under argon to give $Ta(C_2H_4)(PMe_3)_4Cl$ in high yield. $Ta(C_2H_4)(PMe_3)_4Cl$, like $Ta(CHCMe_3)(PMe_3)_4Cl$, reacts readily with molecular nitrogen to give μ-dinitrogen complexes. The dinitrogen complexes react with HCl to give hydrazine dihydrochloride in high yield and with acetone to give dimethylketazine. The dinitrogen complexes have been labeled with $^{15}N_2$ and studied by ^{15}N NMR and IR spectroscopy.

Introduction

We recently reported some simple μ-dinitrogen complexes of tantalum and niobium which were prepared by reacting neopentylidene complexes with azines.[1] These appear to be best regarded as complexes of N_2^{4-} according to structural investigations[2] and reactions with HCl and acetone which are analogous to those of tantalum and niobium imido complexes.[1] The natural question is whether these or some related μ-N_2 complexes can be prepared by reacting a reduced tantalum or niobium complex with molecular nitrogen. In this paper we show that μ-dinitrogen complexes containing neopentylidene or ethylene ligands can be prepared in this manner but that at least one member of the class of compounds which was prepared via the azine route cannot. Details of the preparation and properties of two new reduced tantalum complexes, $TaCl_3(PMe_3)_3$ and $Ta(C_2H_4)(PMe_3)_4Cl$, are included. Some of these results have appeared in a preliminary communication.[3]

Results

Preparation of Reduced Tantalum Complexes. Tantalum pentachloride is reduced smoothly by sodium amalgam under argon in the presence of excess PMe_3 to give bright red $TaCl_3(PMe_3)_3$ in 80% yield. A cryoscopic molecular weight study shows it to be a monomer. Since two types of PMe_3 resonances are observed in the high-field ^1H NMR spectrum (at δ -6.21 (area 2) and 9.57 (area 1)), $TaCl_3(PMe_3)_3$ is best formulated as an octahedron containing meridional PMe_3 ligands. $TaCl_3(PMe_3)_3$ can also be prepared by heating $Ta_2Cl_6(\text{tetrahydrothiophene})_3$[4] with excess PMe_3 in benzene at 60 °C for 12 h in a sealed tube. To our knowledge $TaCl_3(PMe_3)_3$ is the only simple monomeric adduct of MCl_3 (M = Nb[5] or Ta).

The peculiar chemical shifts of the PMe_3 protons in the ^1H NMR spectrum and the fact that no $^{31}P\{^1H\}$ NMR

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