spectra (MS) were recorded by using a Kratos MS-25 low-resolution instrument under the following conditions: ionizing energy, 70 eV; accelerating potential, 8000 V; trap current, 100 μA; probe temperature, 200-300 °C. The proton nuclear magnetic resonance spectra (^{1}H NMR) were obtained at 60 MHz with a Varian 360-A instrument or at 200 MHz with a Nicolet high-resolution instrument. Samples (30-40 mg) were dissolved in the solvents indicated, and resonances are reported downfield (δ) from the internal tetramethylsilane standard. Elemental analyses were carried out at Galbraith Laboratories, Knoxville, TN. Unless otherwise indicated, the tellurium compounds were handled under red lights and inert atmosphere to minimize photochemical decomposition or autoxidation.

Methyl 9-Telluraheptadecanoate. General Procedure. A mixture of tellurium metal (127 mg, 1 mmol) and 3 mL of distilled H_2O was deaerated and heated at 80 °C in a oil bath under red lights and an argon atmosphere. An argon purged aqueous (1 mL) solution of $NaBH_4$ (100 mg) was added dropwise until a clear, colorless solution of Na-Te-Na was obtained.[11] The mixture was then cooled to room temperature, and 15 mL of an argon purged 1:1 mixture of THF/EtOH containing methyl 8-bromooctanoate (223 mg, 0.95 mmol) and 1-bromooctane (202 mg, 1.05 mmol) was added. The solution was stirred for 60 min under an argon atmosphere, poured into 150 mL of H_2O, and then extracted with three 50-mL portions of ethyl ether. The ether extracts were washed with H_2O (3 × 50 mL), dried (Na_2SO_4), and concentrated in vacuo. The crude product was dissolved in petroleum ether (30-60 °C) and chromatographed on a silicic acid (25 g) column slurried in petroleum ether. The column was initially eluted with ten 25-mL fractions of petroleum ether followed by ten 25-mL fractions of C_6H_6. Aliquots of the fractions were monitored by TLC (solvent C_6H_6), and fractions 13-16 were combined to afford (39%) of methyl 9-telluraheptadecanoate as an oil, TLC, R_f 0.50 (C_6H_6).

Acknowledgment. This research was sponsored by the Office of Health and Environmental Research, U.S. Department of Energy, under Contract W-7405-eng-26, with the Union Carbide Corp. and USPHS Grant HL-27209 from the National Institutes of Health. We thank Linda Ailey for typing the manuscript.

Registry No. **1**, 84057-03-4; **2**, 81815-28-3; **3**, 86374-37-0; **4**, 86374-38-1; **5**, 85976-76-7; Te, 13494-80-9; Na-Te-Na, 12034-41-2; $Br(CH_2)_7CH_3$, 111-83-1; $Br(CH_2)_7COOCH_3$, 26825-92-3; Na-Te-Te-Na, 11089-53-5; p-$IC_6H_4(CH_2)_9I$, 86374-34-7; $CHI{=}CH(CH_2)_3I$, 86374-35-8; $CH_3(CH_2)_3Br$, 109-65-9; $CH{\equiv}C(CH_2)_3I$, 2468-55-5; $I(CH_2)_4COOCH_3$, 14273-88-2; $I(CH_2)_{11}COOCH_3$, 86374-36-9; $Br(CH_2)_{11}COOCH_3$, 26825-95-6.

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(11) As the Te begins to dissolve, the solution initially turns a deep purple or red resulting from the initial formation of sodium ditelluride, Na-Te-Te-Na. As additional Te metal dissolves, the solution becomes progressively lighter until a colorless solution of Na-Te-Na is formed.

Substituent Effects in Cluster Species.[1] 4. Ultraviolet-Photoelectron Spectroscopic and Molecular Orbital Studies of Carbyne Complexes of Multinuclear Cobalt Carbonyls

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Received January 18, 1983

The perturbation of carbyne fragments on being bound to one, two, and three nearest-neighbor cobalt atoms is examined experimentally and theoretically. The former approach results from the development of a photoelectron spectroscopic probe based on the ionization properties of a benzene ring. The latter utilizes Fenske-Hall nonparameterized quantum chemical calculations to analyze the bonding. Both approaches are applied to known carbyne complexes of multinuclear cobalt carbonyls while the latter is also applied to analogous complexes without carbonyl ligands. The two methods give congruent pictures of ligand properties as a function of number of metal atom interactions. A specific conclusion is that the negative charge on a carbyne carbon increases as the number of nearest-neighbor cobalt atoms increases. The implications of this result with respect to carbyne binding to metal surfaces are discussed.

The structure and bonding in transition-metal clusters have been of intense interest to inorganic chemists for some time.[2] An expression of this interest is the on-going search for ligand binding in multinuclear metal systems that differs qualitatively from the binding of the ligand in mononuclear systems. Just as cagelike polyboranes exhibit significantly different properties from monoboranes,[3] so too one expects significant differences in polymetallic clusters relative to mononuclear complexes. In this work we measure the perturbation of ligands bound to multinuclear metal sites as a function of the number of metal-ligand interactions.

The construction of bonding models for multinuclear transition-metal systems is hindered by the sheer size of the problem.[2] On the one hand the strictly calculational approach obscures the solution in a welter of approximate detail,[4] whereas the experimental approach of spectroscopy suffers interpretational problems[5] and is not sufficiently detailed. We have chosen, therefore, to focus attention on the variation of a selected number of parameters through a series of closely related, geometrically characterized

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(1) Part 3: Andersen, E. L.; DeKock, R. L.; Fehlner, T. P. *J. Am. Chem. Soc.* **1980**, *102*, 2644.

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(4) Semiempirical methods of the extended Hückel type are much used in this area.

(5) For example, a bonding model is often used to assign an observed photoelectron spectrum, and, thus, the latter yields no direct information on the bonding.

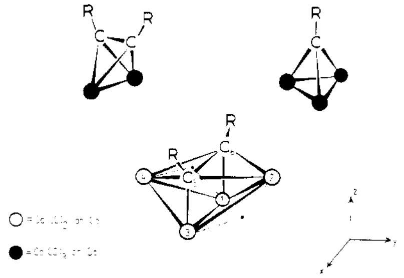

Figure 1. Cobalt carbonyl cluster complexes of carbynes: II, $(CO)_6Co_2(RCCR')$; III, $(CO)_9Co_3(CR)$; IV, $(CO)_{10}Co_4(RCCR')$.

complexes. To do so we develop a photoelectron spectroscopic (PE) substituent probe that yields experimental information on the perturbation of a given ligand on binding to a metal cluster. The probe itself is based on the understanding of substituent effects in the PE spectra of organic moieties as developed by Turner,[6] Heilbronner,[7] and Bock.[8] The development of this probe and the interpretation of the results are aided by the use of the nonparameterized Fenske–Hall calculational method.[9] Again attention is focused on the variation of calculated properties through a series of related molecules.

The systems we have chosen to examine initially involve carbyne fragments bound to cobalt carbonyl clusters containing two, three, and four cobalt atoms, i.e., HCCH (I), $(CO)_6Co_2C_2H_2$ (II), $(CO)_9Co_3CH$ (III), and $(CO)_{10}Co_4C_2H_2$ (IV).[10] These systems, which are illustrated in Figure 1, have all been structurally characterized, can be prepared with a variety of substituents, and are sufficiently volatile so that gas-phase spectra may be obtained. Besides these practical spectroscopic aspects, the interaction of carbynes with multimetal clusters has received considerable attention in recent years because of interest in the cluster–surface analogy.[11] Such studies include PE and LCAO-MO bonding studies of dimetal[12] and trimetal[13] clusters with carbyne ligands. In addition, an X-ray diffraction study of $(C_5H_5Ni)_2C_2H_2$ has provided electron density maps of the acetylene ligand bound to a dinickel cluster.[14] Finally, the existence of numerous experimental[15] and theoretical[16] studies regarding the interaction of carbynes with metal surfaces provides an opportunity to explicitly test the cluster–surface analogy.

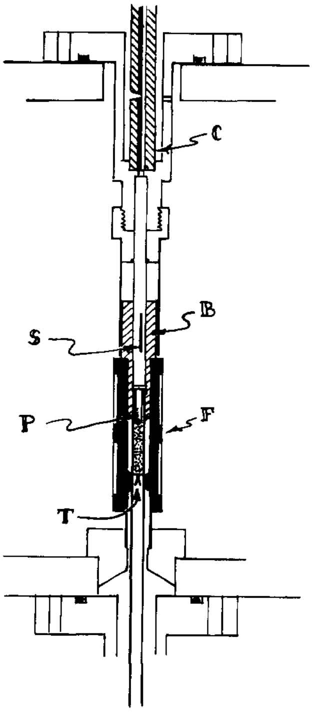

Figure 2. Photoelectron spectrometer source and sample vaporization device: C = He I photon beam collimating capillary: B = copper block; S = source slit; P = quartz crucible holding sample; F = noninductively wound furance; T = thermocouple.

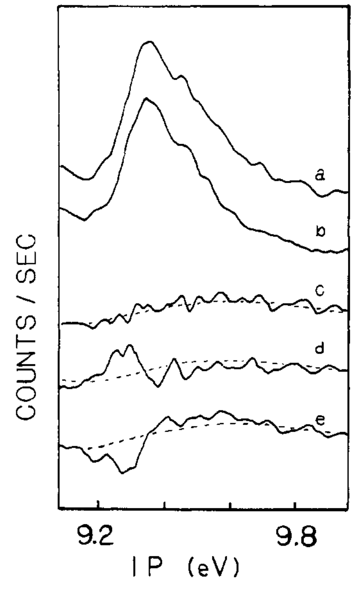

Figure 3. Peak matching of phenyl π ionizations for $CH_3CH_2C_6H_5$ and $HCCC_6H_5$: (a) phenyl π band for $CH_3CH_2C_6H_5$; (b) phenyl π band for $HCCC_6H_5$; (c) difference of a and b; (d) difference of a and b with b shifted 0.024 eV to higher IP; (e) difference of a and b with b shifted 0.024 eV to lower IP. The ionization energy scale refers to spectrum b only.

Experimental Section

Cluster Preparation. The compounds $(CO)_6Co_2(RCCR')$, II (R = H, Ph, R′ = H, Ph), $(CO)_9Co_3CR$, III (R = H, Ph), and

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$(CO)_{10}Co_4(RCCR')$, IV (R = H, Ph, R' = Ph), where Ph = C_6H_5, were prepared and purified by standard literature methods or minor modifications thereof.[17] Characterization was by infrared spectroscopy, and purity was checked by mass spectrometry. Each compounds's vaporization behavior was monitored by using the temperature programmed probe of a computer-controlled mass spectrometer (Du Pont DP-1). This served to demonstrate volatilization of the desired cobalt complex, the onset of significant thermal decomposition, and in general, the optimum conditions for acquiring the desired PE spectra.

Photoelectron Spectroscopy. The present configuration of the PE spectrometer has been described.[18] In order to carry out these and similar studies, an independently, precisely controlled, heated probe was constructed so that solid samples could be vaporized within about 5 mm of the photoionization region (Figure 2). For a test of this sampling device, the spectrum of $Ru_3(CO)_{12}$, a compound previously reported to cause spectrometer drift due to continuous decomposition,[19] was measured. Within experimental error no drift was encountered, and, as evidenced by the absence of a CO PE spectrum, little decomposition occurred. In fact a useful spectrum of $Fe_3(CO)_{12}$ has been obtained with this equipment.[20] The sample is introduced into the spectrometer on the probe via a detachable vacuum lock that permits sample loading in a drybox and sample transfer without exposure to air. Conventional spectra were obtained by using a mixture of Xe and Ar as an internal calibrant. In order to measure the required phenyl π ionizations with greater precision, a simple "peak matching" method was devised. The precision of this method was determined by intercomparing various organic compounds containing the phenyl group. An example is shown in Figure 3. For these ideal cases the measurement of phenyl band position is good to better than ±0.01 eV.

Method of Calculation. Fenske–Hall MO calculations[9] were performed on the IBM 370/168. This method is self-consistent field, and the only necessary input are the basis AO's and the molecular geometry. The basis AO's are the same as those employed in our previous study on $Co_3(CO)_9CCH_3$.[18] That paper also describes the geometry that we used for the tricobalt cluster calculations. For $Co_3(CO)_9CC_6H_5$ the C–C_6H_5 distance was chosen to be 1.44 Å. The geometrical parameters for the $Co_2(CO)_6$ fragment are taken from the X-ray studies of Cotton et al.,[21] after suitable averaging for symmetry purposes. All Co–CO distances are set to 1.80 Å and C–O distances to 1.13 Å as in our tricobalt study. The Co–Co distance is 2.46 Å, and the cobalt–acetylenic carbon distance is 2.00 Å. The C–C acetylenic carbon distance was set at 1.34 Å in the dicobalt hexacarbonyl runs. The C–C_6H_5 distance in the dicobalt compound was 1.42 Å, and C–C distances within the phenyl ring were set at 1.40 Å with C–H distancs in the phenyl ring at 1.08 Å. The same C–H distance was employed for all acetylene calculations on $Co_2(CO)_6$. Bond angles were taken as 99° for Co–Co–CO_{leg} and 152° for Co–Co–CO_{ax}. The CO_{leg}–Co–CO_{leg} angle was set at 104°. Standard angles were chosen within the methyl and phenyl groups of the substituted acetylene ligands. The (substituent)–C–C angle chosen within the acetylene ligand is 145° with the substituent bending away from the $Co_2(CO)_6$ moiety.

The geometry chosen for $Co_4(CO)_{10}C_2H_2$ was an estimated one, based on a partial structure determination.[22] The acetylenic C–C distance was chosen to be 1.436 Å and the C–H distance 1.09 Å; the C–C–H angle was 127°.[23] The wing-tip Co atoms were 2.12 Å removed from the acetylenic carbon atoms and the basal Co atoms were 2.00 Å removed. The basal Co–Co distance was 2.54 Å and basal Co–wing-tip Co was set at 2.48 Å. Two bridging CO groups were assumed. The Co–CO bridge distances are 1.80 Å, and the bridging C–O distance was set at 1.17 Å. Two structures differing in the placement of the bridging CO groups were explored with no significant changes to the results presented herein being in evidence. Calculations on II and IV were completed so that the eigenvectors and population analysis could be analyzed in a basis set of AO's or a basis set utilizing the ten computed MO's of the C_2H_2 molecule (distorted as in the organometallic complex).

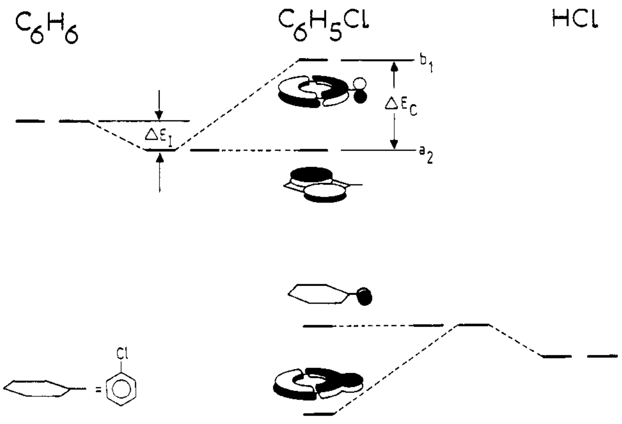

Figure 4. Perturbation model describing the effect of replacing H with Cl on C_6H_6 in terms of ΔE_I (inductive effect of Cl on C_6H_6) and ΔE_c the splitting parameter.

Results and Discussion

Substituent Probe. The major requirement for a useful substituent probe is that the substituent exhibits an ionization characteristic of the substituent (band shape and IP value) that reflects a single parameter of substrate electronic structure. In this section we demonstrate that the phenyl group is such a substituent. The lowest IP of benzene results from the doubly degenerate e_g symmetry π orbitals and is a "sharp" ionization that lies at 9.25 eV.[6] As will be seen below, this IP value is appropriate for studying the cobalt carbonyl clusters. On replacing one hydrogen of benzene with a substituent, e.g., a chlorine atom, the degeneracy is removed and the e_g orbital splits into b_1 and a_2 orbitals by virtue of an interaction with the lone-pair electrons of the Cl atom. Likewise in the PE spectrum of C_6H_5Cl the π ionization is split. This effect in the PE spectrum has been described by using three parameters to model the four IP's involved (see Figure 4).[24] They are the e_g IP of benzene corrected for the inductive effect of the substituent Cl, the Cl lone-pair IP of HCl corrected for the inductive effect of the phenyl ring, and a splitting parameter. The crucial point is that in this model the a_2 IP of C_6H_5Cl relative to the e_g IP of benzene is a measure of the inductive effect of Cl on the phenyl ring. Hence for any substituent X, the change in the a_2 IP will reflect the changing inductive properties of X, which by definition are related to the electronic structure of X.

This analysis has been supported by Fenske–Hall calculations on the free phenylacetylene ligand, the ligand used to probe acetylene binding to cobalt clusters. In Figure 5 the appropriate eigenvalues are shown and it is evident that the qualitative description given above holds for the calculations. More importantly the calculations demonstrate that as the a_2 orbital has a node at the pos-

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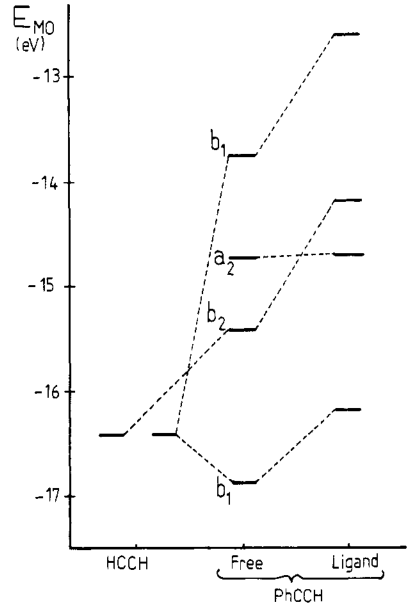

Figure 5. Fenske–Hall description of the perturbation of the π orbitals of acetylene and the highest lying π orbitals of C_6H_6. "Free" refers to the linear structure of $HCCC_6H_5$, whereas "ligand" refers to the structure of $HCCC_6H_5$ as found in the cobalt carbonyl complexes (see Experimental Section).

Table I. Ionization Potentials of the Phenyl a_2 π Orbital for Various Substituents vs. Hammett σ_m Constants

substituent	$IP(a_2)$, eV	σ_m
NH_2	8.94	-0.16
$C(H){=}CH_2$	9.13	
CH_3	9.24	-0.07
H	9.25	
OH	9.28	0.0
$C{\equiv}CH$	9.34	
$C(H){=}O$	9.81	0.38
F	9.82	0.34
NO	9.90	
CN	10.15	0.68

Table II. Comparison of Experimental and Calculated Properties of $C_6H_5CH_2X$ ($X = CH_3, NH_2, OH, H$)

			FH[c]		MNDO[e]	
X	$IP(a_2)$,[a] eV	EN[b]	q_C[d]	$-E(a_2)$, eV	q_C[d]	$-E(a_2)$, eV
CH_3	9.38	2.0	-0.11	14.35	-0.08	9.44
NH_2	9.46	2.9	0.15	14.36	0.12	9.35
OH	9.53	3.5	0.27	14.51	0.20	9.45
H	9.34	2.6	-0.02	14.40	0.08	9.44

[a] This work. Estimated uncertainty ±0.02 eV.
[b] Experimental group electronegativities for X.[42]
[c] Fenske-Hall.[9] [d] Mulliken charge on the benzyl carbon.
[e] Reference 41.

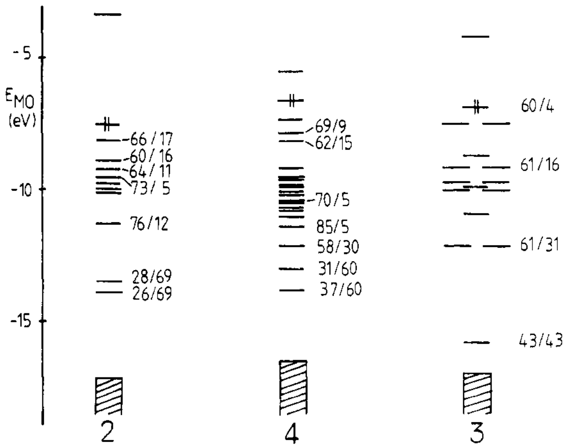

Figure 6. Eigenvalue spectra for cobalt carbonyl complexes of carbynes: 2 refers to $(CO)_6Co_2(HCCH)$; 4 refers to $(CO)_{10}Co_4(HCCH)$; 3 refers to $(CO)_9Co_3(CH)$. The numbers to the right of certain eigenvalues give (percent metal character/percent ligand character).

ition of substitution, it is highly localized on the phenyl substituent and is a measure of the inductive effect of X, i.e., Cl or CCH, on the phenyl ring. The energy of the a_2 orbital in C_6H_5CCH does not depend on geometry, offering evidence that the a_2 orbital is independent of specific orbital interactions. Notice that the acetylenic b_1 and b_2 π orbitals cannot be employed as an indicator of charge on the ligand since distortion of the ligand to "prepare it" for bonding to the metal destabilizes the π orbital by 1.5 eV.

In order to be a practical probe the a_2 IP must be sensitive to changes in electronic structure in the moiety substituted. A survey of the PE spectra of substituted benzenes, Table I, demonstrates that there is a variation in the a_2 IP that may be sensibly correlated with other experimental measures of inductive effect, e.g., the Hammett σ constant. As in this work the atom directly attached to the phenyl ring is always carbon, the series $C_6H_5CH_2X$, where $X = CH_3$, NH_2, OH, and H, has been used to calibrate the method more precisely. These data are given in Table II along with other experimental and theoretical parameters related to inductive effects. Specifically there appears to be a good correlation between the net charge on the CH_2X carbon whether it is estimated from experimental group electronegativities or from Mulliken population analyses of approximate calculations. This is pleasing, but because of the imprecise nature of the term inductive effect, it is not immediately obvious why there should be such a good correlation. Two observations show that a simple correlation as this can only be expected for closely related compounds. First, for X = H (Table II) the correlation is substantially poorer. Second, the calculated Koopmans' a_2 IP's do not sensibly reflect the carbon charges. Clearly, a simple, one electron, molecular explanation will only hold for a series of compounds where final-state effects cancel out. But even in the cases where there is no simple explanation, the a_2 IP does serve as an experimental measure of relative charge on the atom to which it is attached.

General Overview of Cluster Electronic Structures. In this section we compare the basic features of the three cobalt carbonyl clusters shown in Figure 1. The di- and tricobalt systems have been studied[12,13,18] from several points of view, and we emphasize only those points pertinent to our work. The eigenvalue spectra of the clusters for R = H as generated by the Fenske–Hall technique are shown in Figure 6. In all cases there is a group of high-lying orbitals (mainly metal d) followed by the hydrocarbon ligand π-type orbitals and finally the CO-based orbitals plus hydrocarbon σ orbitals. Our interest lies in the first two regions. For these, the orbitals with both significant metal and ligand character are indicated on Figure 6 and it is clear that many of the so-called d orbitals contain considerable ligand orbital character. Some trends through the series are evident. The d bands lie at approximately the same energy but the band width increases with increasing number of cobalt atoms. The HOMO–LUMO gap is largest in the dicobalt system and smallest in the tetracobalt compound. The HOMO in all cases is metal–metal bonding but note that we have previously presented empirical evidence that the lowest cationic state in the dicobalt system results from

Table III. Electronic Charges and Overlap Populations of Carbyne Complexes of Cobalt Carbonyl Clusters by the Fenske-Hall Method

property[a]	$Co_2(CO)_6$-C_2H_2	$Co_4(CO)_{10}C_2H_2$	$Co_3(CO)_9CH$
q_{Co}	−0.05	−0.01[b] 0.14[c]	−0.10
q_C	−0.19	−0.27	−0.40
q_H	0.01	0.00	0.01
M_{CC}	1.46	1.26	
M_{CH}	0.86	0.88	0.88
M_{CoC}	0.18	0.45 (3-5)[d] 0.10 (5-2) 0.11 (5-4)	0.50
M_{CoCo}	0.07	0.14 (1-3)[d] 0.03 (3-2) 0.13 (3-4)	0.11

[a] Electronic charge is indicated by the symbol *q* and overlap populations by *M*. [b] Hinge atom. [c] Wing-tip atom. [d] Numbering scheme given in Figure 1.

ionization of an orbital that contains significant ligand character.[25]

We turn next to a survey of the calculated atomic charges and overlap populations obtained with the Mulliken analysis[26] and contained in Table III. The metal atoms are all nearly neutral in charge; however, a d orbital only charge analysis would indicate a metal charge of about 1.0. Since the metal 4s and 4p orbitals may be too diffuse, even with the exponents that are employed, we suggest that the actual charge is positive. This agrees with the ab initio calculated charge on the dicobalt compound of 1.25; a calculation that did not use 4p orbitals on the Co atoms.[12d] The carbyne carbon charges are all negative and progressively more so in the order dicobalt, tetracobalt, and tricobalt (vide infra). The overlap populations between a given Co atom and a carbyne carbon atom are small but vary significantly between the three compounds. The Co–Co overlap populations are very small, and the small values observed in general for M–M interactions have been recently discussed.[27]

The general validity of these calculations is supported, and the major effects of phenyl substitution are revealed by an examination of the series of dicobalt photoelectron spectra shown in Figure 7. In the region 8–17 eV the spectrum of $Co_2(CO)_8$ exhibits simply a d band at ca. 8–10 eV and a CO band at ca. 13–16 eV with an open "window" between 10 and 13 eV. $(CO)_6Co_2C_2H_2$ exhibits similar bands plus a band in this window (11 eV) which is easily assigned to the acetylene ligand π ionizations. Addition of one phenyl substituent results in the addition of several bands all of which are similar to those found for benzene itself. By comparison, then, the band at about 9.3 eV is assigned to the phenyl π ionizations. Confirmation of this assignment results from an analysis of the relative intensity changes on going to the diphenyl derivative. Note that the phenyl π band lies in the open window of the unsubstituted cluster at the expected IP and the band has the characteristic shape associated with phenyl π ionizations, i.e., a very sharp leading edge. The same analysis carried out for the tricobalt system leads to the same result. For the tetracobalt compound only the phenyl and diphenyl derivatives have been examined; however, location of the phenyl π band is straight forward.

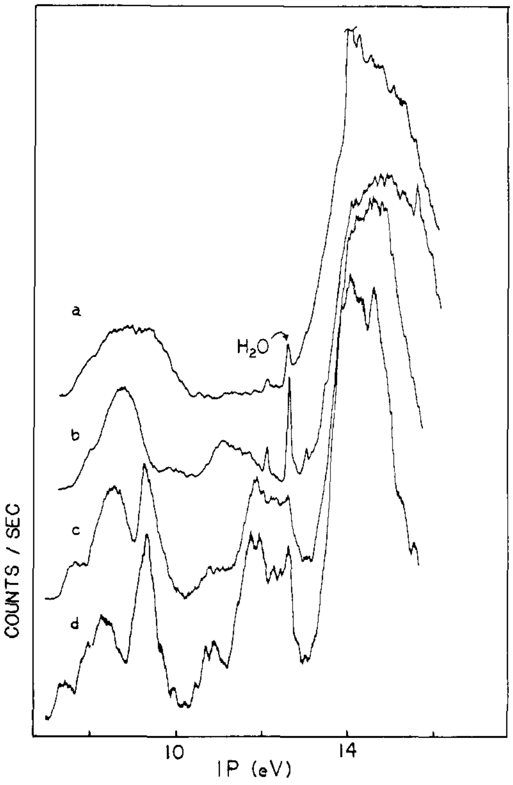

Figure 7. He I photoelectron spectra of cobalt carbonyl complexes: (a) $Co_2(CO)_8$; (b) $(CO)_6Co_2(HCCH)$; (c) $(CO)_6Co_2(HCCPh)$; (d) $(CO)_6Co_2(PhCCPh)$.

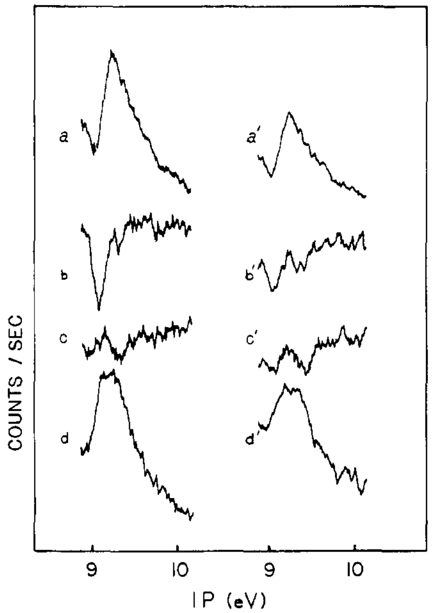

Figure 8. Peak matching of phenyl π bands: (a) $(CO)_6Co_2(HCCPh)$; (d) $(CO)_9Co_3CPh$; (b) a–d with Xe voltage markers matched; (c) a–d with d shifted 0.090 eV to higher IP; (a′) $(CO)_6Co_2(HCCPh)$; (d′) $(CO)_{10}Co_4(HCCPh)$; (b′) a′–d′ with Xe voltage markers matched; (c′) a′–d′ with d′ shifted 0.04 eV to higher IP. (Note this is one of several measurements.)

The Phenyl Probe. Experimental. In Figure 8 the phenyl π regions of the PE spectra of II, III, and IV are shown and, as illustrated, peak matching by difference is used to establish a_2 IP differences. Matching of all possible pairs, with diphenyl derivatives as well as free ligands, has been carried out, and these results are given in Table IV. The results on I, II, and III have the highest precision while that on IV suffers from a poor signal to noise ratio. Despite

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[25] DeKock, R. L.; Lubben, T. V.; Hwang, J. L.-S.; Fehlner, T. P. *Inorg. Chem.* **1981**, *20*, 1627.

[26] Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.

[27] Rives, A. B.; Xiao-Zeng, Y.; Fenske, R. F. *Inorg. Chem.* **1982**, *21*, 2286.

Table IV. Comparison of Experimental and Calculated Properties of Carbyne Complexes of Cobalt Carbonyl Clusters

molecule	IP(a_2), eV	$-E(a_2)$,[a] eV	electronic charge FH[a]	electronic charge EH[b]	electronic charge ESCA[c]
HCCH			−0.05	−0.12	
C_6H_5CCH	9.56	14.73	0.06[d]		
			0.17		
$Co_2(CO)_6(C_2H_2)$			−0.19	−0.26	−0.2 ± 0.3
$Co_2(CO)_6(C_6H_5CCH)$	9.28	13.71	−0.10[d]		
			−0.22		
$Co_3(CO)_9CH$			−0.40	−0.60	−0.5 ± 0.2
$Co_3(CO)_9CC_6H_5$	9.18	13.63	−0.35		
$Co_4(CO)_{10}(C_2H_2)$			−0.27	−0.36	
$Co_4(CO)_{10}(C_6H_5CCH)$	9.25				

[a] Fenske-Hall. [b] Extended Huckel. [c] Reference 13d. [d] Carbyne carbon attached to the phenyl ring.

this, the results on the latter are sufficiently good to establish that the a_2 IP lies between those for II and III.

The data in Table IV demonstrate that it becomes increasingly easier to remove an electron from a localized π orbital of a phenyl group attached to a carbyne carbon as the number of cobalt atoms per carbyne carbon in the cluster increases. Either the inductive effect of the (carbyne)cobalt cluster unit increases the shielding of the phenyl carbons as the number of cobalts per carbyne carbon increase, or the charge flow to the hole localized on the phenyl ring in the ion state increases as the number of cobalts per carbyne carbon increase, or the explanation is a combination of the two. On the basis of the discussion of the calibration of the technique above, we suggest that the trend of decreasing a_2 IP's is also the trend of increasing negative charge on the carbyne carbon, i.e., an increasingly positive inductive effect as the number of cobalts per carbyne carbon increases. This interpretation is in agreement with an independent, contemporary, study[13d] of compounds II and III in which the ESCA C 1s binding energies of the carbyne carbons were measured. The calculated charges from this work are included in Table IV where it is seen that the carbyne carbon of III is more negative than that of II. The electron-rich character of the carbyne carbon in III is also supported by the interpretation of deformation density maps obtained from X-ray diffraction studies.[28]

Theoretical. Support for this interpretation results from Fenske–Hall calculations on I–IV as well as the phenyl-substituted I–III. First the trend in carbyne carbon Mulliken charge (Table IV) is the same as that deduced from the experimental measurements for both the substituted as well as unsubstituted compounds. In addition, charges derived from extended Hückel calculations,[10] though not the same, exhibit a similar trend. Second, in this closely related series of molecules even the calculated Koopmans' a_2 IP's correlate with the measured IP's.

A more detailed examination of the calculated MO properties yields a description of the phenyl substituent effect in this metal system congruent to that described above for organic molecules. First, the electronic charges and overlap populations (Table V) demonstrate a small but definite substituent effect of the phenyl group on the cluster itself. However, the changes in these properties on substitution are essentially equal for II and III. This supports our contention that differences measured by the phenyl substituent reflect real differences in the unsubstituted cluster complex; i.e., they are not introduced by the substituent itself. Second, the eigenvalue spectra for II and III are shown in Figure 9. The d bands undergo only minor changes upon substitution. The two MO's in II derived from the π orbitals of acetylene are perturbed by mono- and diphenyl substitution in effectively the same qualitative fashion as in the free ligand.[29] Likewise the same region of the eigenvalue spectrum of III shows the splitting of the two C 2p metal triangle "π" orbitals[18] and the removal of the degeneracy of the benzene π orbitals.

Table V. Electronic Charges and Overlap Populations for Phenyl-Substituted Carbyne Complexes of Cobalt Carbonyl Clusters by the Fenske-Hall Method

Δproperty[a]	$Co_2(CO)_6C_2(Ph)_2$	$Co_3(CO)_9CPh$
Δq_{Co}	−0.03	−0.01
Δq_C	0.06	0.05
Δq_{Ph}	−0.05	−0.05
ΔM_{CC}	−0.01	
ΔM_{CPh}	0.15	0.13
ΔM_{CoC}	−0.01	−0.02
ΔM_{CoCo}	0.01	0.01

[a] Difference between the indicated property and that for the H-substituted compound in Table III.

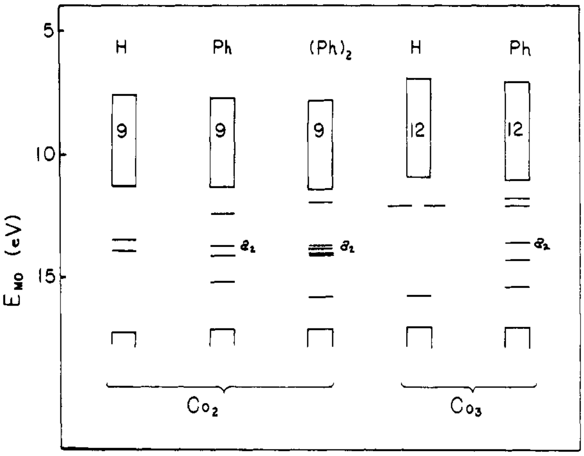

Figure 9. Calculated eigenvalue spectra of $(CO)_6Co_2(HCCH)$, $(CO)_6Co_2(HCCPh)$, $(CO)_6Co_2(PhCCPh)$, $(CO)_9Co_3CH$, and $(CO)_9Co_3CPh$.

There is one significant difference between the spectroscopic and calculated results. Comparison of the PE spectrum (Figure 7) and the calculated eigenvalue spectrum (Figure 9) for $(CO)_6Co_2(HCCPh)$ shows a discrepancy in the calculated position of the a_2,b_1-derived orbitals of the phenyl substituent. The calculation places these orbitals in the acetylenic π orbital region, whereas experimentally the a_2 orbital is assigned to a band that lies to higher binding energy than the d band. Note that the

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[28] Leung, P.; Holladay, A.; Coppens, P. "Abstracts of Papers", 181st National Meeting of the American Chemical Society, Atlanta, GA, Apr 1981; American Chemical Society: Washington, DC, 1981; INOR 90.

[29] Carlier, P.; Mouvier, G. *J. Electron Spectrosc. Relat. Phenomen.* **1979**, *16*, 169. Andreocci, M. V.; Bicev, P.; Cauletti, C.; Piancastelli, M. N. *Gazz. Chim. Ital.* **1980**, *110*, 31.

calculated a_2–b_1 splitting (Figure 5) is much larger than the splitting measured experimentally (0.96 vs. 0.59 eV for phenylacetylene) and that the calculated splitting increases upon bending phenyl acetylene into the ligand geometry. However, in the cobalt derivatives the relative band intensities (Figures 7 and 8) strongly suggest that both the a_2 and b_1 IP's lie in the single band heretofore described as the phenyl π band. This empirical assignment is supported by the slight splitting of the phenyl π band of III (Figure 8).

As far as this work is concerned, the difference between theory and experiment puts our interpretation of the phenyl π band measurements in jeopardy as our assumption is that we measure the a_2 IP and not the b_1. Several factors suggest that the measurements are validly interpreted. First, in terms of interpreting PE spectra the Fenske–Hall calculations exaggerate the a_2–b_1 splitting partly because the acetylene π and phenyl π orbitals are calculated to be similar in energy in contrast to the different experimental IP's. Second, as the perturbing group moves farther from the ring, the a_2 and b_1 IP's merge; i.e., both a_2 and b_1 reflect only inductive effects.[30] Third, in II, for example, the direct interaction of the b_1 with the acetylene orbitals is partially cancelled by an analogous interaction with the acetylene π^*–cobalt d interaction orbital.[25] This shows up in the calculations as a decrease in the b_1–a_2 gap from 2.2 eV in phenylacetylene (bent) to 1.3 eV in the dicobalt derivative. Fourth, the largest a_2–b_1 PE splitting should occur for III as experimentally the phenyl π ionizations lie close to the C $2p\pi$–Co_3 ionizations. In this case the calculations predict, probably correctly, a_2 over b_1, i.e., a_2 at lower IP. Our conclusions are that in II, the a_2 and b_1 IP's are experimentally indistinguishable and that in III the a_2 IP is the lowest IP. Hence, the interpretation of the phenyl π band measurements is correct. We have no calculational evidence concerning the interpretation of the phenyl substituent effect in IV but assume that the a_2–b_1 splitting is small here as well.

Back-Bonding with Cluster Size. The presently accepted model of the bonding of unsaturated organic molecules to transition-metal atoms is based upon that of Dewar–Chatt–Duncanson.[31] Applied to a mononuclear metal system, this bonding model focuses on the donation of electrons from the π orbital of the organic molecule and back-donation of metal d electron density to the π^* orbital of the ligand. The distortion of the ligand, C–C bond lengthening and the bending away of substituents from the metal, is thought to enhance metal–ligand bonding via better ligand-to-metal π donation as well as metal-to-ligand π^* back-donation. Numerous theoretical studies have examined the bonding of ethylene and acetylene to metal centers.[32]

Interaction of alkyne ligands with multimetal clusters has received considerable attention and II and IV have been often mentioned as models for C–C bond lengthening as the number of metals in the metal–ligand interaction increases.[11] The calculations carried out in conjunction with this study allow us to explore in more detail the similarities and differences between II and IV. Note that II contains the acetylene ligand in a μ configuration while IV has the acetylene in a μ orientation with respect to the wing-tip cobalt atoms and a di-σ orientation with the hinge cobalt atoms. In order to make the connection between II and IV more smoothly, we have carried out an additional calculation on $Co_2(CO)_6C_2H_2$ with the acetylene ligand oriented on the dimetal moeity in a di-σ fashion.[33] For this calculation the acetylene ligand geometry was left unchanged (C–C = 1.34 Å, CCH = 145°). The ligand was raised so that after the 90° rotation, the Co–C bond remained at 2.0 Å. The electron occupations in the four acetylene π-type orbitals are listed in Table VI for the three calculations of interest here. The calculated carbon atom charges (q_C) on the acetylene ligand are also tabulated.

Table VI. π-Electron Occupations[a]

	Co_2-(μ-C_2H_2)	Co_2-(di-σ-C_2H_2)	$Co_4C_2H_2$
q_C	−0.19	−0.19	−0.27
π_{total}	4.22	4.31	4.35
π^*_{xy}	0.35	0.11	0.37
π^*_z	0.60	0.77	0.95
π_z	1.70	1.51	1.46
π_{xy}	1.57	1.92	1.57

[a] All calculations refer to the organometallic complexes with CO ligands. See Figure 1 for definition of coordinate system.

We note first that q_C does not change in comparing the di-σ and μ orientations for $Co_2(CO)_6C_2H_2$. However, the total number of π electrons increases by 0.09 electron upon going from the μ to the di-σ orientation. This indicates that a corresponding decrease of 0.09 electron took place in the σ-bonding framework of the ligand. For $Co_4(CO)_{10}C_2H_2$, q_C is more negative by 0.08 electron and the total π-electron population on the ligand is greater by 0.13 electron compared to $Co_2(CO)_6(\mu$-$C_2H_2)$. Therefore, at least for the two experimentally known molecules, the difference in charge on the carbon atom is due to the π-electron occupations and not the σ orbitals of the ligand.

We turn now to the individual π-electron occupations for the three calculations shown in Table VI. For the $Co_2(CO)_6C_2H_2$ molecules, changing from a μ orientation to a di-σ orientation results in decreased participation of the π_{xy} and π^*_{xy} orbitals in bonding to the metals. This is reflected in a population near 2 for π_{xy} and near 0 for π^*_{xy}. However, the opposite effect occurs in the π_z and π^*_z set of orbitals. The π_z population has dropped to 1.51 and the π^*_z population has increased to 0.77.

We can continue our analysis by going from $Co_2(CO)_6$(di-σ-C_2H_2) to $Co_4(CO)_{10}C_2H_2$. The major effect here is the addition of two wing-tip cobalt atoms which should have a major impact on the populations of the π_{xy} and π^*_{xy} orbitals. This expectation is based on the fact that the spatial orientations of the π_{xy} and π^*_{xy} orbitals is in the direction of the wing-tip cobalt atoms. Our expectation is borne out upon examination of the populations given in the table. The π_{xy} population decreases by 0.35 and the π^*_{xy} population increases by 0.26 electron. At the same time, there are smaller but still significant changes occurring in the π_z and π^*_z populations. These changes also are in such a direction as to indicate increased participation of the ligand with the Co_4 cluster compared to the Co_2 cluster in its hypothetical di-σ configuration. This in turn leads to a decrease in the C–C overlap populations and an increase in the carbon electronic charge. Cluster complex III is in a sense the limiting situation with a C–C bond

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[30] Compare for example the spectra of C_6H_5X with $C_6H_5CH_2X$.[24]

[31] Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C71. Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.

[32] Blizzard, A. C.; Santry, D. P. *J. Am. Chem. Soc.* **1968**, *90*, 5749. McWeeny, R.; Mason, R.; Towl, A. D. C. *Faraday Discuss. Chem. Soc.* **1969**, *47*, 20. Hay, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 5226. Kitaura, K.; Sakaki, S.; Morokuma, K. *Inorg. Chem.* **1981**, *20*, 2292. Calabro, D. C.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 6846. Tatsumi, K.; Hoffmann, R.; Templeton, J. L. *Inorg. Chem.* **1982**, *21*, 468. Mingos, D. M. P. *Adv. Organomet. Chem.* **1977**, *15*, 1.

[33] See: Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858.

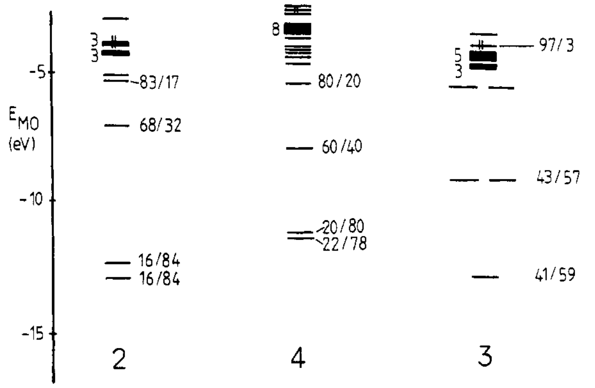

Figure 10. Eigenvalue spectra of $Co_2(HCCH)$, $Co_4(HCCH)$, and Co_3CH with the structures shown in Figure 1. The numbers have the same meaning as those in Figure 6.

Table VII. Electronic Charges and Overlap Populations of Carbyne Complexes of Cobalt Clusters by the Fenske-Hall Method

property[a]	$Co_2C_2H_2$	$Co_4C_2H_2$	Co_3CH
q_{Co}	0.33	0.09,[b] 0.32	0.26
q_C	−0.35	−0.41	−0.82
q_H	0.02	−0.01	0.05
M_{CC}	1.46	1.32	...
M_{CH}	0.86	0.91	0.88
M_{CoC}	0.16	0.42 (3-5)[d] 0.07 (4-5)[d]	0.51
M_{CoCo}	0.09	0.02 (1-3)[d] 0.12 (1-4)[d]	0.08

[a] For symbolism, see footnote to Table III. [b] Hinge cobalt. [c] Wing-tip cobalt. [d] Number scheme in Figure 1.

order of zero and the highest carbon charge.

Role of the Carbonyl Ligands. The carbonyl ligands in II, III, and IV serve to "preserve" the clusters or to terminate the exo-cluster valencies of the cobalt atoms not involved in bonding the hydrocarbon. They can, clearly, affect the cluster–hydrocarbon interaction and, thus, stand as one of the larger caveats to the assumption of these systems as valid models for hydrocarbon bonding to metal surfaces or to small metal-bare clusters.[34] With calculational chemistry it is of course possible to remove the CO ligands from II–IV and examine the changes in the metal–hydrocarbon interaction. We have done so with the Fenske–Hall technique, and the pertinent results are summarized in Figure 10 and Table VII.

Comparison of the eigenvalue spectra of the bare clusters (Figure 10) with those for the carbonyl clusters shows a few interesting trends. First in the bare systems the d band is much narrower and at higher energy. (There is, of course, no CO band.) Second, the ligand character is focused in fewer orbitals, specifically four for each molecule, and, thus, there is much less mixing with the d band orbitals. For II and IV the four metal–ligand orbitals correlate with the ligand π and π* orbitals, whereas for III the three major metal–ligand orbitals correlate with a CH σ orbital and the CH 2pπ orbitals.[35] The qualitative MO picture of the metal–ligand interaction orbitals is similar to that for the carbonyl clusters discussed above and elsewhere.[12,13]

The same holds true if one compares calculated properties of the bare clusters (Table VII) with those for the carbonyl clusters (Table III). There are only trivial changes in the overlap populations, and although the charges are different (cobalt more positive, carbon more negative), the trend in the carbon charges is the same as that for the carbonyl clusters. This is emphasized in Figure 11 where calculated charges for both types of clusters are plotted vs. a_2 IP. Thus, although the net calculated charge transferred to a carbyne carbon depends on the presence or absence of carbonyl ligands, the change in this parameter depends on the number of nearest-neighbor metal atoms and is independent of the carbonyls. Note (Figure 11) that simple (noniterative) extended Hückel calculations,[10] parameterized to yield reasonable results on the carbonyl clusters, do not reproduce these charge trends and must be considered suspect as far as other aspects of the electronic structure of the bare clusters are concerned.

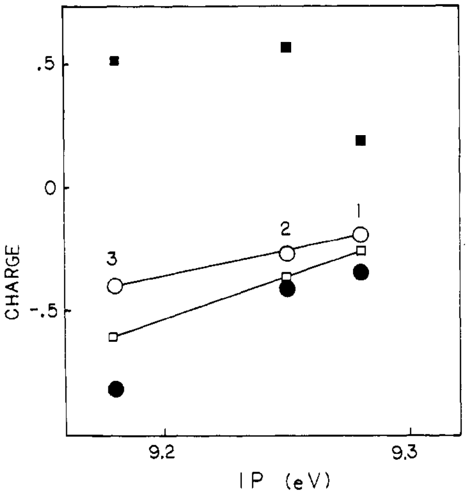

Figure 11. Plot of the Mulliken charge vs. the a_2 IP for the cobalt carbyne clusters. The numbers refer to the number of nearest-neighbor cobalt atoms per carbyne carbon. The circles are for charges calculated with the Fenske–Hall method with open circles for the carbonyl clusters and closed for the bare clusters. The squares are for extended Hückel calculations with open squares for the carbonyl clusters and closed for the bare clusters. For both Hückel calculations the parameterization is the same.[10]

Implications for Surface-Bound Hydrocarbons. Our results provoke some questions concerning the behavior of alkynes on metal surfaces. The measurement of work function changes on adsorption of a variety of species on metal surfaces has been used extensively as a means to probe the electronic changes caused by the adsorption process.[36,37] Specifically, the work function change has been coupled to charge transfer between the admolecule and the metal surface. Simply put this charge transfer establishes a surface dipole which either causes a reduction or increase in the work function of the metal. With this model ligand-to-metal charge transfer predicts a decrease in the work function while metal-to-ligand transfer predicts an increase.[36] Hence the observed negative work function changes on the adsorption of alkynes have been interpreted in terms of alkyne to metal charge transfer.[38] In fact, organic ligands on metal surfaces have been viewed as possessing carbonium ion character.[39] Our results demonstrate metal-to-ligand charge transfer in the carbonyl

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(34) Moskovito, M. *Acc. Chem. Res.* **1979**, *12*, 229.

(35) The designations π and σ here refer to rotation around the C_3 symmetry axis. Their proper notations in C_{3v} symmetry are e and a_1, respectively.

(36) Somorjai, G. A. "Chemistry in Two Dimensions: Surfaces"; Cornell University Press: Ithaca, NY, 1981.

(37) Rhodin, T. N.; Ertl, G. "The Nature of the Surface Chemical Bond"; North Holland: New York, 1979.

(38) See, for example: Nieuwenhuys, B. E. *Surf. Sci.* **1981**, *105*, 505. P. C. Stair, *J. Am. Chem. Soc.* **1982** *104*, 4044.

(39) Mason, R.; Thomas, K. M. *Anal. N.Y. Acad. Sci.* **1974**, *239*, 225. Clarke, T. A.; Gay, I. D.; Mason, R. In "Physical Basis for Heterogeneous Catalysis"; Drauglis, E., Jaffe, R. I., Eds.; Plenum Press: New York, 1975.

clusters and enhanced metal-to-ligand charge transfer in the bare clusters. Calculations were also carried out on a Co_4 clusters having the geometry of IV. The HOMO for Co_4 is found to be -2.5 eV while that for $Co_4C_2H_2$ is -2.8 eV demonstrating that in the cluster systems the "work function" does correlate with calculated charge transfer. Thus, the cluster model systems would suggest *carbanion* character for bound acetylenes on metal surfaces. We must conclude that either the cluster systems used here do not model a surface in a very fundamental fashion or the work function changes have been incorrectly interpreted.

Recently, Shustorovich[40] has pointed out that the simple surface dipole model for explaining work function changes is incomplete and cannot explain paradoxical work function changes (work function change negative and metal-to-ligand charge transfer). He has suggested that not only does the nature of the admolecule–surface metal dipole have to be considered but an internal surface dipole must be taken into account as well; i.e., a type of double layer is set up on adsorption. Such considerations show that chemisorption of an electronegative adatom can result in either an increase or decrease in the work function depending on the natures of the atom and metal. Presumably similar considerations hold for admolecules. Most likely, then, the cluster systems studied here do correctly model the charge-transfer aspects of alkyne adsorption on metal surfaces in accord with intuitive chemical concepts of electronegativity differences between carbyne carbons and transition metals. In addition, it seems clear from this work that the greater the number of transition-metal atoms that can be associated with a carbyne carbon at a given metal site, the greater the net charge transfer to the carbyne carbon atom.

Acknowledgment. The support of the National Science Foundation under Grant CHE 79-15220 is gratefully acknowledged. We thank the University of Notre Dame Computing Center for providing computing time.

Registry No. $C_6H_5CH_2CH_3$, 100-41-4; $C_6H_5CH_2NH_2$, 100-46-9; $C_6H_5CH_2OH$, 100-51-6; $C_6H_5CH_3$, 108-88-3; HCCH, 74-86-2; C_6H_5CCH, 536-74-3; $Co_2(CO)_6(C_2H_2)$, 12264-05-0; $Co_2(CO)_6(C_6H_5CCH)$, 12154-91-5; $Co_3(CO)_9CH$, 15664-75-2; $Co_3(CO)_9CC_6H_5$, 13682-03-6; $Co_4(CO)_{10}(C_2H_2)$, 12282-40-5; $Co_4(CO)_{10}(C_6H_5CCH)$, 12568-53-5; $Co_2(CO)_6C_2(Ph)_2$, 14515-69-6.

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(40) Shustorovich, E. *Solid State Commun.* **1981,** *38,* 493. Shustorovich, E.; Baetzold, R. C. *Appl. Surf. Sci.* **1982,** *11/12,* 693. Shustorovich, E. *J. Phys. Chem.* **1982,** *86,* 3114.

(41) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977,** *99,* 4899. Thiel, W. *QCPE* **1978,** *11,* 353.

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Complexes of $(C_6F_5)_2Co$ and $(C_6F_5)_2Ni$. Synthesis of (η^6-Arene)bis(pentafluorophenyl)cobalt(II) Using Cobalt Atoms. Reactions, η^6-Arene Lability, and Use in Synthesis of Tetrahedral $(C_6F_5)_2Co(L)_2$

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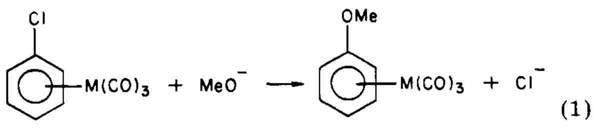
The high lability of the η^6-arene ligand in $(C_6F_5)_2Co(\eta^6\text{-arene})$ has been used to advantage to prepare new $(C_6F_5)_2Co(L)_2$ and $(C_6F_5)_2Co(L\text{-}L)$ complexes (L = tetrahydrofuran, tetrahydrothiophene, and pyridine and L-L = bipyridine). According to spectral and magnetic data these are tetrahedral compounds. Similar π-arene displacements on $(C_6F_5)_2Ni(\eta^6\text{-arene})$ have yielded square-planar *trans*-$(C_6F_5)_2Ni(L)_2$ and square-planar *cis*-$(C_6F_5)_2Ni(L\text{-}L)$. The starting cobalt–arene complex induced the polymerization of norbornadiene and propyne. Thermolysis of the starting complex led to free radical decomposition, which is contrasted by nonradical reductive coupling with the nickel analogue. η^6-Arene-exchange equilibria for the cobalt- and nickel–arene complexes indicated the order of preference for η^6-arenes as mesitylene > toluene > benzene > anisole for cobalt and mesitylene > toluene ≈ anisole > benzene for nickel. A literature background regarding monoarene complexes is presented.

Background

The first mono(arene)metal complexes were reported in 1958.[1-4] Upon complexation, the properties of the arene change significantly. For example, some nucleophilic displacements became facile (e.g., eq 1). The potential



(1)

synthetic utility of this reaction prompted investigations of ways of cleaving the M–arene bond to release the new arene. Pyridine and phosphines worked well,[4] but the products were not easily converted back to arenes such that M could be reused. Natta and co-workers[2] and Nicholls and Whiting[3,4] reported greater than 60% yields of (η^6-*N,N*-dimethylaniline)$Cr(CO)_3$ from the reaction of (η^6-

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(1) Fischer, E. O.; Öfele, K. *Z. Naturforsch, B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1958,** *13B,* 458.

(2) Natta, G.; Calderazzo, F.; Santambrogio, E. *Chim Ind. (Milan)* **1958,** *40,* 1003.

(3) Nichols, B.; Whiting, M. C. *Proc. Chem. Soc., London* **1958,** 152.

(4) Nichols, B.; Whiting, M. C. *J. Chem. Soc.* **1959,** 551.