

$W(\text{CHCMe}_3)(\text{H})\text{Cl}_3\text{L}_2$ reacts with carbon monoxide as shown in eq 2 and with 2 equiv of PMe_3 as shown in eq 3. $W(\text{CHCMe}_3)(\text{H})\text{Cl}_3\text{L}_2 + \text{CO} \rightarrow W(\text{CHCMe}_3)(\text{CO})\text{Cl}_2\text{L}_2^{13} + \text{HCl}$ (2)

$W(\text{CHCMe}_3)(\text{H})\text{Cl}_3\text{L}_2 + 2\text{PMe}_3 \rightarrow W(\text{CCMe}_3)(\text{H})\text{Cl}_2\text{L}_3^{14} + \text{Me}_3\text{PH}^+\text{Cl}^-$ (3)

$(\text{CCMe}_3)(\text{H})\text{Cl}_2\text{L}_3$ appears to be analogous with $W(\text{CH})(\text{H})\text{Cl}_2\text{L}_3$.⁷ It reacts with CO to yield $W(\text{CHCMe}_3)(\text{CO})\text{Cl}_2\text{L}_2$ and free PMe_3 . NMR studies suggest that the PMe_3 ligands in $W(\text{CHCMe}_3)(\text{CO})\text{Cl}_2\text{L}_2$ are mutually trans and that the neopentylidene ligand is again one of the severely distorted variety ($\delta_{\text{C}_\alpha} = 240$, $J_{\text{CH}_\alpha} = 73$ Hz). The carbonyl absorption was observed at 1935 cm^{-1} in the IR spectrum.

The structure^{15,16} of $W(\text{CHCMe}_3)(\text{CO})\text{Cl}_2(\text{PMe}_3)_2$ is shown in Figures 1 and 2. The geometry about the central tungsten(IV) atom may be regarded as intermediate between distorted octahedral and capped octahedral. Within the distorted octahedral description, the trans angles are $\text{Cl1-W-C2} = 156.37$ (11)°, $\text{Cl2-W-C1} = 169.02$ (11)°, and $\text{P1-W-P2} = 165.46$ (3)°, while cis angles range from $\text{Cl1-W-C1} = 78.36$ (11)° through $\text{Cl2-W-C2} = 110.67$ (11)°. The α -hydrogen atom of the neopentylidene ligand, H2, lies over the $\text{P1}\cdots\text{Cl2}\cdots\text{C2}$ face in a capping position (see figure 2). The tungsten-alkylidene distance, W-C2 , is 1.859 (4) Å, the C2-H2 distance is 1.053 (36) Å, and the $\text{W}\cdots\text{H2}$ distance is only 1.835 (36) Å, indicative of a substantial metal-hydrogen interaction. The W=C2-C3 angle is 168.7 (3)°, while $\text{W=C2-H2} = 72.2$ (20)° and $\text{H2}\cdots\text{W-C2} = 33.1$ (11)°. The neopentylidene ligand is one of the most distorted observed to date by structural studies (cf. $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{CHCMe}_3)(\text{PMe}_3)(\text{C}_2\text{H}_4)$,^{5a} where $\text{Ta=C}_\alpha\text{-H}_\alpha = 78.1$ (3)°, $\text{Ta}\cdots\text{H}_\alpha = 2.042$ (5) Å, $J_{\text{CH}_\alpha} = 74$ Hz). Note that the tungsten(VI) species $W(\text{O})(\text{CHCMe}_3)\text{Cl}_2(\text{PEt}_3)$ has $\text{W=C}_\alpha = 1.882$ (14) Å and $\text{W=C}_\alpha\text{-C}_\beta = 140.6$ (11)°, with no evidence for any substantial $\text{W}\cdots\text{H}_\alpha$ interaction.^{4b}

The capped octahedral face is the largest of the eight possible octahedral faces and is defined by the angles $\text{Cl2-W-C2} = 110.67$ (11)°, $\text{P1-W-C2} = 103.69$ (11)°, and $\text{Cl2-W-P1} = 89.38$ (3)°. The octahedral face opposite the capped face is associated with the same essential ligand atoms (Cl, P, C) but smaller interligand angles, viz., $\text{Cl1-W-C1} = 78.36$ (11)°, $\text{Cl1-W-P2} = 82.25$ (3)°, and $\text{P2-W-C1} = 97.25$ (11)°.

$W(\text{CHCMe}_3)(\text{H})\text{Cl}_3\text{L}_2$ and $W(\text{CCMe}_3)(\text{H})\text{Cl}_2\text{L}_3$ also react with ethylene (slowly) to give $W(\text{CHCMe}_3)(\text{C}_2\text{H}_4)\text{Cl}_2(\text{PMe}_3)_2$.¹⁷ Its ¹³C NMR spectrum shows that the neopentylidene ligand is similar to that in $W(\text{CHCMe}_3)(\text{CO})\text{Cl}_2(\text{PMe}_3)_2$ ($\delta_{\text{C}_\alpha} = 237$, $J_{\text{CH}_\alpha} = 70$ Hz) and that only one type of ethylene carbon atom is present ($\delta_{\text{C}} = 36$, $J_{\text{CH}} = 154$ Hz). Since two sets of ethylene protons are found at 1.85 and 1.74 ppm, the ethylene probably lies along the

P-W-P axis in a structure analogous with that found for $W(\text{CHCMe}_3)(\text{CO})\text{Cl}_2(\text{PMe}_3)_2$.

We believe these three neopentylidene complexes are important for several reasons. First, they illustrate what appears to be a trend toward alkylidene hydride complexes in the absence of good π -donor ligands. Since H_α in $W(\text{CHCMe}_3)(\text{CO})\text{Cl}_2(\text{PMe}_3)_2$ is interacting substantially with the metal (1.835 (36) Å), the W=C2-C3 angle is large (168.7 (3)°), and the W=C_α bond length is short (1.859 (4) Å), one could argue that it is essentially a neopentylidene hydride complex. This result is consistent with recent results in the chemistry of "reduced" tantalum^{5a} and tungsten¹⁸ neopentylidene complexes. Second, carbon monoxide is found to bind to a metal that one could argue is in a fairly high oxidation state and, further, does not react with the alkylidene ligand to form a ketene ligand, a type of reaction that appears common for certain tantalum and niobium alkylidene complexes.¹⁹ Third, in a related vein, an olefin is found to be compatible with a "reduced alkylidene" complex, in keeping with recent results for tantalum²⁰ and niobium,²¹ suggesting that *undistorted* alkylidene ligands, especially in tungsten(VI) oxo and imido complexes, are those characteristic of a system that will metathesize olefins. Fourth, the fact that HCl evolves when $W(\text{CHCMe}_3)(\text{H})\text{Cl}_3(\text{PMe}_3)_2$ is treated with carbon monoxide or ethylene suggests that this may be an important, heretofore unrecognized, means of forming tungsten-carbon multiple bonds.

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Registry No. 1, 80679-42-1; $W(\text{CHCMe}_3)(\text{CO})\text{Cl}_2(\text{PMe}_3)_2$, 80679-43-2; $W(\text{CHCMe}_3)(\text{C}_2\text{H}_4)\text{Cl}_2(\text{PMe}_3)_2$, 80679-44-3; $W(\text{CCMe}_3)\text{Cl}_3(\text{PMe}_3)_2$, 80679-45-4; $W(\text{CCMe}_3)\text{Cl}_3(\text{PMe}_3)_3$, 80679-46-5.

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Photoelectron Spectroscopic Measurements of the Relative Charge on Carbyne Fragments Bound to Polynuclear Cobalt Carbonyl Clusters

Prabodh Deshmukh, T. K. Dutta, J. L.-S. Hwang, C. E. Housecroft, and T. P. Fehlner*

Department of Chemistry, University of Notre Dame
Notre Dame, Indiana 46556

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Definition of the changes in the internal bonding of an organic ad molecule on being bound to a metal surface is the driving force behind much contemporary physical and chemical research.¹ Analogies drawn between organometallic chemistry and organic reactions on surfaces ("surface organometallic chemistry")² provide one fruitful avenue of approach in that metal cluster fragments are thought to usefully mimic metal surfaces.³ This is particularly true insofar as the covalent interaction of a ligand with two or more metals is concerned, and structures of multinuclear transition-metal clusters have been suggested as models for binding sites on actual metal surfaces.⁴ Further, transfor-

(13) Anal. Calcd for $\text{WC}_{12}\text{H}_{28}\text{Cl}_2\text{P}_2\text{O}$: C, 28.54; H, 5.59. Found: C, 28.50; H, 5.62.

(14) Anal. Calcd for $\text{WC}_{14}\text{H}_{37}\text{Cl}_2\text{P}_2$: C, 30.40; H, 6.74. Found: C, 30.81; H, 6.86. δ_{C_α} (C_6D_6) = 285 (q, $^2J_{\text{CP}} = 15$ Hz, $J_{\text{CW}} = 205$ Hz); δ_{WH} (toluene- d_6) = 3.86 (q, $^2J_{\text{HP}} = 73$ Hz, $J_{\text{HW}} = 18$ Hz); $\delta_{\text{PA}} \approx -2.3$, $\delta_{\text{PB}} \approx -9.7$, $\delta_{\text{PC}} \approx -20.5$ ($J_{\text{AB}} = 46$ Hz, $J_{\text{AC}} = 137$ Hz, $J_{\text{BC}} = 54$ Hz).

(15) $W(\text{CHCMe}_3)(\text{CO})\text{Cl}_2(\text{PMe}_3)_2$ crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with $a = 15.460$ (3) Å, $b = 9.795$ (1) Å, $c = 12.923$ (2) Å, $\beta = 90.66$ (1)°, $V = 1956.8$ (5) Å³, $Z = 4$. Single-crystal X-ray diffraction data ($M\alpha$ radiation) were collected by using a coupled θ - 2θ scan technique¹⁶ on a Syntex $P2_1$ diffractometer. A combination of Patterson and difference-Fourier techniques allowed the location of all atoms, including all 28 hydrogen atoms in the molecule. Full-matrix least-squares refinement led to $R_F = 2.6\%$ and $R_{wF} = 2.3\%$ for all 3471 reflections with $3.5^\circ \leq 2\theta \leq 50.0^\circ$ (not one datum rejected).

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

X	IP of a_2 , ^a eV	EN ^b	FH ^c		MNDO ^e	
			q_C ^d	$-\epsilon_{a_2}$, eV	q_C	$-\epsilon_{a_2}$, eV
CH ₃	9.38	2.0	-0.11	14.35	-0.077	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

^a This work. ^b Experimental group electronegativities for X, ref 9. ^c Fenske-Hall, ref 10. ^d Mulliken charge on the benzylic carbon. ^e Reference 11.

mations of organic fragments on metal clusters are thought to mirror similar transformations on surfaces.⁵ In the following we report the measured changes in the ionization behavior of a carbyne carbon substituent as a function of the number of transition-metal nearest neighbors in a series of cobalt clusters. It is demonstrated that these measurements define a trend in carbyne carbon charge as a function of metal environment. As charge distribution reflects the nature of the bonding and is a primary ingredient in determining reactivity, these measurements provide further detailed information on the cluster-surface analogy.

In earlier work we demonstrated that the relative electronic charge of an atom in a series of related compounds may be monitored by measuring the ionization potential of a filled orbital forced by symmetry to be localized on an appropriate substituent at the atom in question.⁶ For practical reasons, in this work we have used a phenyl substituent rather than the halogen substituents used previously. On replacement of one hydrogen of a benzene ring with another group, the high-lying $e_g\pi$ orbital is split into a_2 and b_1 components.⁷ As the a_2 orbital has a node at the position of substitution, it is effectively localized on the benzene ring. Thus, the a_2 orbital energy should reflect only the inductive effect of the fragment to which it is attached and, within the confines of Koopmans' Theorem,⁸ the a_2 ionization potential (IP) should be as well. To test this supposition, the a_2 IP's for $C_6H_5CH_2X$, where $X = CH_3, NH_2$, and OH , have been measured by UV photoelectron spectroscopy (UV-PES). These data, given in Table I, as well as other such correlations, demonstrate that the effect of CH_2X on the a_2 phenyl IP reflects both experimental and theoretical expectations of the net charge on the CH_2X carbon. However, the explanation for this correlation cannot be attributed only to an inductive effect on the ground state of the molecule as the calculated Koopmans' a_2 IP's (Table I) do not sensibly reflect the carbon charges. Despite the lack of a simple, one-electron, molecular explanation of why the a_2 IP vs. charge correlation exists, the measurements show that the phenyl substituent can serve as an experimental probe of relative charge. In fact the a_2 IP contains information similar to that provided by core IP's⁹ but has the high sensitivity that facilitates the acquisition of gas-phase spectra of compounds of low volatility. Experimentally the approach is practical because the phenyl π IP's have sharp onsets and, for metal carbonyl clusters, appear in an open region of the spectrum above the d ionizations and below other ligand ionizations.¹² In addition, for the metal compounds studied, the a_2 IP occurs below the b_1 IP, permitting the precise measurement of the former. An advantage of the

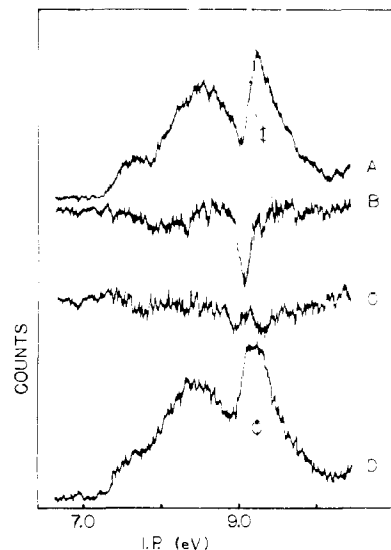


Figure 1. Lowest IP bands of the gas-phase He(I) photoelectron spectra of (A) $C_6H_5CHCo_2(CO)_6$ and (D) $C_6H_5CCo_3(CO)_9$, with the CO bands adjusted to approximately the same intensity (the phenyl π bands are marked); (B) difference of spectra A and D with the Xe reference line at 12.13 eV matched; (C) difference of spectra A and D with spectrum A shifted 0.10 eV to lower ionization energy.

Table II. Phenyl Ionizations and Calculated Carbyne Carbon Charges

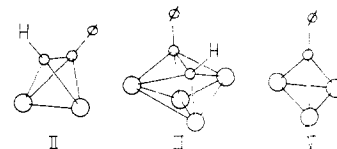
compound	IP of a_2 , ^a eV	q_C ^b
	R = C_6H_5	R = H
RCCH	9.56	-0.12
(RCCH)Co ₂ (CO) ₆	9.28	-0.26
(RCCH)Co ₄ (CO) ₁₀	9.25	-0.36
(RC)Co ₃ (CO) ₉	9.18	-0.60

^a Estimated uncertainty in IP differences = ± 0.02 eV.

^b Mulliken charge of carbyne carbon from an extended Hückel calculation.

distinctive phenyl π -ionization behavior is that only a rudimentary assignment of the UV-PES is required, and this spectral assignment is completely independent of quantum chemical calculations. Thus, in principle, this method could be applied to surface studies where calculations are very difficult. The main disadvantages of the method are low sensitivity to charge and the necessity of comparing compounds that are closely related.

The phenyl substituent probe has been initially applied to the series C_6H_5CCH (I), $(C_6H_5CCH)Co_2(CO)_6$ (II),^{13,14} $(C_6H_5CC-H)Co_4(CO)_{10}$ (III),^{15,16} and $(C_6H_5C)Co_3(CO)_9$ (IV),^{17,18} each of



which has been structurally characterized, albeit with different alkyne substituents.¹⁹ In addition, the electronic structures of I, II, and IV have been previously studied both theoretically and

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experimentally.^{7,20,21} Figure 1 shows the pertinent region of the gas-phase photoelectron spectra²² of II and IV and illustrates the "peak-matching" technique used to measure the a_2 IP's given in Table II. At minimum the results in Table II demonstrate that it becomes progressively 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. Based on our earlier work and the data in Table I, we suggest that these IP's also demonstrate increasing negative charge on the carbyne carbon as the a_2 IP decreases. This suggestion is in accord with the decreasing trend in C-C bond order for I, II, and III as reflected by the measured C-C distances.⁴ It is also in accord with Mulliken charge analyses of extended Hückel calculations on I, II, III, and IV.²³ These are given in Table II, where it is seen that there is a smooth increase in the relative carbyne carbon negative charge as the number of cobalt atoms per carbyne carbon increases.²⁴

The generally accepted model for coordination of acetylene to a transition metal involves $\pi \rightarrow M$ and $M \rightarrow \pi^*$ charge transfer.²⁵ A net transfer of electron density either from or to the acetylene ligand will cause an increase in the C-C bond distance (and reduction in bond order) due to either a net depopulation of the bonding π orbital or a net population of the antibonding π^* orbital. The results of this work on I, II, and III demonstrate that for cobalt there is a net back-donation into the π^* orbital of the ligand, which increases as the number of metal atoms to which the acetylene is bound increases. The measurement on IV suggests that the highest negative charge on carbon is achieved by cleaving the C-C bond thereby increasing the proportion of metal nearest neighbors to the carbon. Insofar as the behavior of these clusters model the interactions of acetylene with a metal surface, the results suggest that the fairly facile cleavage of alkynes on metals is due to charge transfer from the metal to carbon,²⁷ and those sites permitting the greatest number of metal-carbyne carbon interactions will be the most effective in carrying out the cleavage.

The measured work function changes on adsorption of acetylene on various metals are negative and have been interpreted as involving ligand to metal charge transfer.^{1,28} However, it has been pointed out that there exist conditions where even the adsorption of an electronegative atom on a metal surface can yield a negative work-function change.²⁹ Assuming the carbonyl cobalt clusters studied here do model an important aspect of surface bonding, we suggest that acetylene as an admolecule also produces a paradoxical change in the metal work function. Work on related

systems is underway, and a complete account of this work will appear elsewhere.

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Registry No. I, 536-74-3; II, 12154-91-5; III, 12568-53-5; IV, 20756-47-2; $C_6H_5CH_2CH_3$, 100-41-4; $C_6H_5CH_2NH_2$, 100-46-9; $C_6H_5C-H_2OH$, 100-51-6.

High Optical Yields in a Photochemical Cycloaddition. Lack of Cooperativity as a Clue to Mechanism

Laren M. Tolbert* and Mahfuza B. Ali

Department of Chemistry, University of Kentucky
Lexington, Kentucky 40506-0055

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High optical yields in photochemical asymmetric induction through 2 + 2 cycloaddition can be obtained when the conformations leading to chiral products are rigidly enforced. Most commonly such conformations are enforced by maintaining the cycloaddends in a chiral crystal lattice,¹ although optical yields up to 86% have been obtained in solution by enforcing the conformation with an intervening chiral chain connecting the cycloaddends.² The extensive π overlap and resulting rigidity apparent in the exciplex of *trans*-stilbene and dimethyl fumarate (1), which produces almost exclusively dimethyl μ -truxinate (2) despite the greater stability of the all *trans* isomer dimethyl δ -truxinate (3) (see Figure 1),³ suggested this system as a model in solution for the geometry imposed by the crystal state. Furthermore, the possibility of alternative reaction paths, one involving stepwise bond formation, the other concerted bond formation, made available a further application of the principle of cooperativity in asymmetric induction.⁴

The stereoselectivity of dimethyl μ -truxinate formation requires an intimate relationship between the phenyl groups and carboxyalkyl groups of the cycloaddends (see Figure 2). We reasoned that fumarate derivatives with chiral alcohols as prosthetic groups should exhibit substantial selectivity for one prochiral face of the stilbene excited state, leading to exciplex formation, and that the resulting cycloadduct should exhibit a large enantiomeric excess.⁵ In order to test this hypothesis, we synthesized methyl *l*-bornyl fumarate (4), di-*l*-bornyl fumarate (5),⁶ methyl (*R*)-2-methyl-1-butyl fumarate (6), and bis((*R*)-2-methyl-1-butyl) fumarate (7) and investigated the unsensitized photocycloaddition to stilbene. The resulting cycloadducts were produced in high optical yields, in one case reaching 90-94%.

Irradiations of 0.06 M benzene solutions of *trans*-stilbene in the presence of the optically active esters (0.06 M) were carried out with a 450-W medium-pressure mercury lamp with Corex filter. The reactions were monitored by gas chromatography and

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(6) Methyl *l*-bornyl fumarate, a colorless liquid, was synthesized from *l*-borneol and the monomethyl ester of fumaryl chloride. Di-*l*-bornyl fumarate, mp 106-108 °C, was synthesized from *l*-borneol and fumaryl chloride. Methyl (*R*)-2-methyl-1-butyl fumarate and bis((*R*)-2-methyl-1-butyl) fumarate were similarly prepared as colorless liquids. All new compounds gave satisfactory elemental analyses.