Molecular Orbital Calculations on Octahedral Carbyne Complexes: Bonding, Structure Deformations, and Frontier-Controlled Nucleophilic Additions

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Nonparametrized Fenske–Hall molecular orbital calculations were carried out on *trans*-$XCr(CO)_4CR$ (X = Cl, Br, I; R = Me, Ph, NEt_2), *trans*-$PMe_3Cr(CO)_4CMe^+$, *mer*-$BrCr(CO)_3(PMe_3)CMe$, various isomers of $BrCr(CO)_2(CNMe)_2CPh$ and $BrCr(CO)_2[P(OH)_3]_2CPh$, and *trans*(PH_3)-$(PH_3)_2(CO)_2FeCPh^+$. The two Cr–C(carbyne) π bonds are equivalent in the tetracarbonyl complexes containing CMe^+, slightly nonequivalent in the complexes with CPh^+, and greatly different in the complexes with $CNEt_2^+$ ligand. This change is evident in the molecular orbital energies, metal–ligand overlap populations, and ligand orbital populations. The Cr–C(carbyne)–R units in most complexes are slightly bent because of the low symmetry of the carbyne π-electron clouds, crystal packing forces, and nonbonding interactions. Carbynes seem to be stronger π acceptors than CO, $CNEt_2^+$ being weaker than CMe^+ and CPh^+. The calculations indicate that halogens do not use their p_π orbitals for bonding to chromium. Equatorial CO ligands are displaced toward the axial halogen atom. We attribute this to direct donation from the halogen p_σ orbital into the 2π orbitals of carbonyl ligands, not to steric strain. The trans position of the halogen and carbyne ligands and the observed configurations of disubstituted complexes do not seem to be due to bonding. The calculated electronic structures may be verified by photoelectron spectroscopy. The only neutral chromium complex reported to add nucleophiles to its carbyne carbon atom is the only one whose LUMO corresponds to a Cr–C(carbyne) π antibond. This finding corroborates our claim that nucleophilic additions to carbyne ligands are frontier controlled rather than charge controlled. Addition of H^- to *trans*(PPh_3)-$(PPh_3)_2$-$(CO)_2OsCC_6H_4Me$-p^+ also seems to be frontier controlled. On the basis of calculations, we propose experiments by which new frontier-controlled reactions of carbyne complexes may be discovered.

Introduction

Multiple metal–ligand bonds greatly influence the properties and behavior of coordination and organometallic complexes. Experimental and theoretical studies of multiple bonding have often been difficult, sometimes even controversial. If the symmetry of an ensemble of ligands around the metal atom is sufficiently high, σ and π interactions do not mix appreciably. Such separation makes the discussion of bonding easier. This is why we chose to study novel octahedral carbyne complexes of chromium, which, by electron-counting rules, contain triple metal–carbon bonds. We also discuss briefly an iron-containing model of a trigonal-bipyramidal compound of osmium, the only known carbyne complex with that geometry.

This work represents the second part of our theoretical study of electronic structure, bonding, reactivity, and geometry of carbyne complexes. The first part[1] dealt with metal–carbyne bonds in several $CpMn(CO)_2CR^+$ (Cp = η^5-C_5H_5) and $ArCr(CO)_2CPh^+$ (Ar = η^6-aryl) complexes and in $(CO)_5CrCNEt_2^+$. We offered a general explanation, in terms of frontier control, for addition of many nucleophiles to these complexes. In this paper we further discuss triple metal–carbon bonds, examine bonding of chromium with other ligands in the carbyne complexes, discuss orientation in substitution of CO ligands, and recognize new examples of frontier-controlled nucleophilic addition to the carbyne carbon.

Details of Calculations

An approximation to the Hartree–Fock–Roothaan technique, the Fenske–Hall self-consistent field (SCF) method has been described elsewhere[2] and some of its applications have been reviewed.[3,4] The method is devoid of adjustable parameters so that the results of a calculation (eigenvectors and eigenvalues) are completely determined by the geometry of the molecule and by the nature and size of the atomic basis set. To expedite calculations on the large molecules, we used $P(OH)_3$, PH_3, MeNC, and CPh^+ as models of ligands $P(OPh)_3$, PPh_3, *t*-BuNC, and CC_6H_4Me-p^+, respectively. Comparative calculations on the real ligands and their models did not reveal any significant differences in the electronic structures and bonding abilities that would be attributable to substitution of hydrogen atoms for larger groups. We therefore believe that these simplifications, routinely made in nonrigorous as well as in ab initio molecular orbital calculations, are justified. The basis functions for heavy atom osmium are not available, and we used the basis functions of iron instead. Since the validity of this approximation is uncertain, our discussion of the osmium carbyne complex will be brief. The orbital populations and atomic charges are calculated by the Mulliken population analysis.

Basis Sets. The term basis function, as used in this paper and elsewhere, corresponds to a distinct pair of *n* and *l* quantum numbers. For example, a 3p function comprises three 3p orbitals. The atomic functions for Cr, C, H, O, and N were the same ones used in the first part of our study.[1] The functions 1s through 4s for Fe were taken from the tables[5] and function 4p had 1.60 as its exponent. Single-ζ forms were used for all functions of phosphorus except for 3p, whose double-ζ coefficients were 1.243 and 2.071.[6] The "best atom" functions were used for halogens.[7]

Structures. We took geometries of most carbyne complexes from the known crystal structures, determined by Fischer, Huttner, Frank, and their co-workers: ICr-

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$(CO)_4CMe$,[8,9] $ClCr(CO)_4CPh$,[10] $BrCr(CO)_4CPh$,[8,10] $BrCr(CO)_4CNEt_2$,[8,11,12] *mer*-$BrCr(CO)_3(PMe_3)CMe$,[8,9] *trans*-(CO)-$BrCr(CO)_2[P(OPh)_3]_2CPh$,[8,13] *cis*(CO)-$BrCr(CO)_2$(*t*-$BuNC)_2CPh$,[8,13] and *trans*-$[PMe_3Cr(CO)_4CMe]BCl_4$.[8] The halogen and carbyne ligands are trans to each other in every complex. We chose bond lengths in the remaining few carbyne complexes on the basis of the known structures mentioned above and several other related ones.[14,15] The bond angles at Cr were 90° in most calculations, and we base our discussions on these results. In several exploratory calculations, equatorial CO ligands were bent toward the halogen atom by 3°. We assumed the five-coordinate complex $(PPh_3)_2(CO)_2OsCC_6H_4Me$-$p^+$ to be trigonal bipyramidal with axial phosphines on the x axis and with the tolyl group and the carbonyl ligands in the equatorial (yz) plane and calculated the bond lengths in the iron model from the known structures of closely related carbyne[16] and vinylidene[17] complexes. In every complex molecule the right-hand coordinate system is centered at the metal atom, with the z axis pointing toward the carbyne carbon atom.

Bonding Abilities of the Fragments

We partitioned each octahedral molecule into the metal atom and the ligands; when there was more than one ligand of the same kind, we treated them as a single fragment. This approach permitted simultaneous examination of all metal-ligand bonds and allowed for ligand-ligand interactions. The trigonal-bipyramidal molecule consisted of two fragments—the metal-containing moiety and the carbyne—so that only the metal–carbyne bonding could be examined. After the SCF portion of a calculation would converge in the atomic basis set, the molecular orbitals were transformed into a basis of metal and ligand (or ligand fragment) orbitals. Partitioning and basis transformation made the bonding clearer without changing the results of the calculations.

Carbynes. In order to simplify description of bonding, we treated carbyne fragments as ions CR^+, which have even numbers of electrons. Of course, such redistribution of electrons among the fragments does not affect the results of calculations on complete molecules. A detailed account of electronic structures and bonding capacities of carbynes can be found in our first paper,[1] so only the salient features will be summarized here.

The highest occupied molecular orbital (HOMO) in every carbyne ligand is labeled σ and corresponds to a lone pair in an sp hybrid orbital, localized on the carbyne carbon atom. The three carbyne ligands have different low-lying empty orbitals. In CMe^+, the two degenerate lowest unoccupied molecular orbitals (LUMO's), labeled π, are practically pure p orbitals of the carbyne carbon atom. The LUMO in CPh^+, designated 4π, is perpendicular to the phenyl ring and delocalized over its ortho and para positions, as in benzyl species. This delocalization somewhat stabilizes the LUMO relative to the next lowest unoccupied molecular orbital, marked 5π, which is essentially a p orbital of the carbyne carbon atom in the ring plane. In $CNEt_2^+$, extensive mixing occurs between one p orbital of carbon and the p orbital (lone pair) of trigonal nitrogen, which are both perpendicular to the ligand plane. Their in-phase combination is the principal constituent of molecular orbital 1π, which corresponds to a C–N π bond. The LUMO, designated $2\pi_c$, is an almost pure in-plane p orbital of the carbyne carbon atom. The next lowest unoccupied orbital, 3π, has much higher energy than the LUMO because it is an out-of-phase p_C–p_N combination, i.e., a C–N π antibond. The results of an extended Hückel calculation on CNH_2^+ agree with the above description.[18]

These three carbyne ligands constitute a unique series. When attached to a metal fragment that contains degenerate π-donating orbitals, CMe^+ will form two equivalent π bonds with the metal, CPh^+ will make two similar but not equivalent bonds, and $CNEt_2^+$ will create two very different π bonds with the metal. The two π systems in the same molecule will be orthogonal in each case. If the symmetry of the metal fragment is too low to permit a doubly degenerate π level, the bonding with carbynes will become even more complicated.[1]

Other Fragments. The CO ligand binds to a transition metal mainly through its frontier orbitals: the σ-donating 5σ (a carbon lone pair) and two degenerate π-accepting orbitals 2π; the latter are antibonding within the ligand.[19] This mode of bonding is preserved when the fragments $(CO)_2$, $(CO)_3$, and $(CO)_4$ are used. The levels derived from individual 5σ orbitals are filled and the high-energy levels made from the 2π orbitals of individual carbonyls are empty in the free fragments.

The PMe_3 ligand has a phosphorus-localized σ orbital as its HOMO. The next highest filled level is 7 eV below the HOMO and consists of two degenerate hyperconjugative orbitals of e symmetry; these orbitals can be viewed as combinations of the phosphorus p orbitals with the P–C σ bonds. The doubly degenerate LUMO level is high in energy. The electronic structure of PH_3 is analogous to that of PMe_3. Ligand $P(OH)_3$ is similar to these two ligands except its LUMO level is much lower in energy.

The MeNC ligand has a carbon-localized σ orbital (its lone pair) as the HOMO, two degenerate C–N π-bonding orbitals below it, and two degenerate LUMO's as their C–N π-antibonding counterparts. This set of five orbitals is isolated in energy from the lower lying occupied and from the higher lying vacant molecular orbitals.[20] The electronic structures of the phosphines and isocyanides will be discussed again in connection with the reactivity of carbyne complexes.

The bonding abilities of fragment $(PH_3)_2(CO)_2Fe$ are similar to those of $Fe(CO)_4$, examined elsewhere.[21] A set of five orbitals, largely localized on the iron atom, is isolated in energy from other orbitals. The highest three orbitals in this set are as follows: π_{xz}, almost a pure d_{xz}

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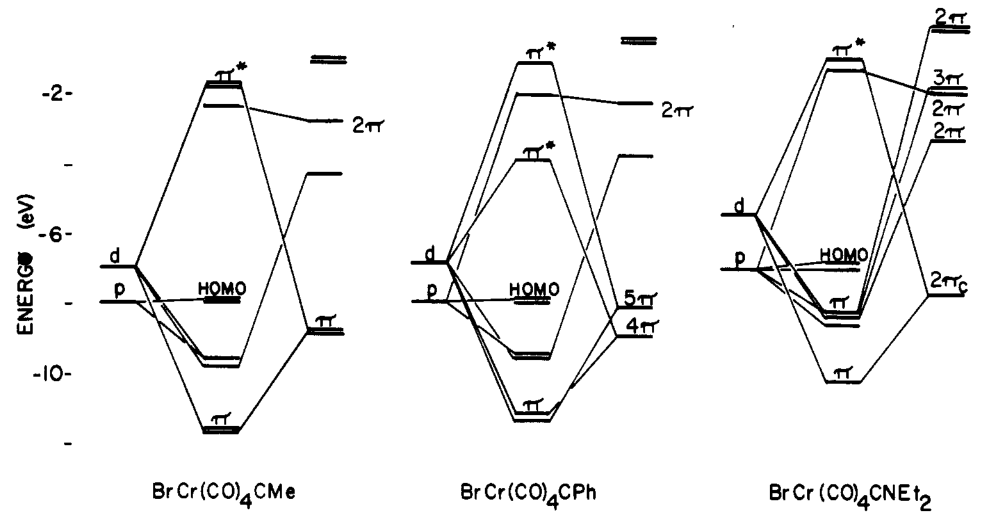

Figure 1. Molecular orbital diagrams for *trans*-$BrCr(CO)_4CR$ (R = Me, Ph, NEt_2). The second $Cr–CNEt_2$ π antibond has high energy and is not shown. Labels of the fragment orbitals: d for Cr 3d, p for Br 4p, 2π for the lowest four 2π-derived levels of $(CO)_4$, π for CMe^+, 4π and 5π for CPh^+, and $2\pi_c$ and 3π for $CNEt_2^+$.

Table I. Energies and Percent Compositions of Important MO's in *trans*-$BrCr(CO)_4CMe$

	Cr					CMe		$(CO)_4$		Br
ε, eV	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	$d_{xz,yz}$	4p	σ	π	5σ	2π	4p
−1.69[a]				34			54		8	
−2.31 (LUMO)	9								63	22
−7.85 (HOMO's)[a]										98
−9.49	8				12				7	70
−9.66			58						40	
−11.48[a]				43			38		14	
−17.61		39						54		
−17.63	29				7			50		
−17.85[a]					21			73		
−19.75						13		65		

[a] Doubly degenerate level.

Table II. Energies and Percent Compositions of Important MO's in *trans*-$BrCr(CO)_4CPh$

	Cr					CPh			$(CO)_4$		Br
ε, eV	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	$d_{xz,yz}$	4p	σ	4π	5π	5σ	2π	4p
−3.76 (LUMO)				32			42			7	
−7.80 (HOMO)											98
−7.82											98
−9.39	8				12					6	71
−9.42			61							38	
−11.13				38			46			11	
−11.27				45				37		13	
−14.47							lower MO				
−15.17							lower MO				
−16.80	17				4	56					
−17.60		39							56		

orbital of Fe; the HOMO (π_{yz}), a combination of 60% of d_{yz} and 20% of p_y of Fe; and the LUMO, designated 2σ. The two filled orbitals of the fragment can donate electrons to the low-lying empty carbyne orbitals, whereas the empty orbital 2σ can accept electron density from the HOMO σ of a carbyne ligand.

Bonding in the Complexes

All energies of fragment orbitals in Figures 1–3 are diagonal elements of the Fock matrices from the calculations on complete carbyne complexes. These energies reflect the influences of the molecular environment upon the fragments "ready for bonding". In the discussions of bonding we will emphasize metal–ligand π interactions. The metal–ligand σ-bonding orbitals have such low energies that most of them are not shown in the molecular orbital diagrams.

***trans*-$BrCr(CO)_4CR$ (R = Me, Ph, NEt_2).** Comparison of these three compounds (Figure 1 and Tables I–III) shows how the electronic structure of a complex depends on the bonding ability of the carbyne ligand in it. The HOMO in each complex is practically pure p_π orbital of Br; the highest occupied level is doubly degenerate in the complex containing CMe^+, but in other two complexes, whose overall symmetries are lower, the splitting occurs.

Chromium–carbyne π interactions are particularly interesting. Even without calculations on the fragment $BrCr(CO)_4$, it is clear that it has two equivalent π-donating orbitals (mainly d_{xz} and d_{yz} atomic orbitals of Cr). Their interactions with two equivalent π orbitals of CMe^+ give rise to an essentially doubly degenerate level at −11.48 eV. Each d_π–π overlap population is 0.269; this relatively large positive number indicates that these two π interactions are bonding. Since the two π-accepting orbitals of CPh^+ (4π

Table III. Energies and Percent Compositions of Important MO's in *trans*-$BrCr(CO)_4CNEt_2$

	Cr					$CNEt_2$				$(CO)_4$		Br
ϵ, eV	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	$d_{xz,yz}$	4p	1π	σ	2π	3π	5σ	2π	4p
−0.94				34				52			11	
−1.35 (LUMO)	9				4						65	20
−6.77 (HOMO)				9					5			84
−6.97												98
−8.16				46					18		17	16
−8.34			46								43	
−8.52	9				11						7	71
−10.20			40					41			14	
−15.43					7	58				24		
−16.40		38								56		
−16.97								4		72		20
−17.16					14	28				51		
−17.34	28				6		31					

Table IV. Populations of Crucial Ligand Orbitals in *trans*-$BrCr(CO)_4CR$ Complexes

	CR			average CO		Br	
R	HOMO σ	LUMO	next lowest orbital	5σ	2π	p_σ	p_π
Me	1.33	0.92	0.92	1.44	0.39	1.39	3.97
Ph	1.38	1.07	0.88	1.45	0.36	1.42	3.96
NEt_2	1.39	0.96	0.50	1.46	0.43	1.42	3.98

Table V. Energies and Percent Compositions of Important High-Lying MO's in *trans*-$ClCr(CO)_4CMe$

	Cr					CMe	$(CO)_4$	Cl
ϵ, eV	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	$d_{xz,yz}$	4p	π	2π	3p
−8.64 (HOMO's)[a]								97
−9.83			59				40	
−10.27	7				11		5	74
−11.69[a]				42		37	14	

[a] Doubly degenerate level.

and 5π) are not equivalent, the two Cr–C π-bonding molecular orbitals (at −11.13 and −11.27 eV, respectively) are not degenerate. The overlap populations of d_π with 4π and 5π are 0.225 and 0.279, respectively. The greater overlap population corresponds to the more stable molecular orbital. Since the $2\pi_c$ and 3π orbitals in $CNEt_2^+$ are very different, the two Cr–C π-bonding molecular orbitals in the complex are widely separated: −10.20 and −8.16 eV. Respective overlap populations between the chromium d_π and the $2\pi_c$ and 3π orbitals of $CNEt_2^+$ are 0.259 and 0.180. The π-bonding orbitals discussed so far have unoccupied π-antibonding counterparts, which are shown in Figure 1. In the later discussion of reactivity it will be important to notice that the LUMO in *trans*-$BrCr(CO)_4CPh$ is π antibonding between chromium and carbyne.

On the basis of Kettle's symmetry arguments,[22] the Cr–C–Me unit in the octahedral carbyne complexes should be linear, whereas the Cr–C–Ph and Cr–C–NEt_2 units should be bent. Indeed, data in Table IV show that the electron cloud is cylindrically symmetrical in CMe and unsymmetrical in CPh and $CNEt_2$ ligands. The observed bond angles in the solids confirm the influence of the symmetry-dictated chromium–carbyne bonding upon the geometries but reveal some effects of crystal forces as well. The Cr–C–R moiety is linear in the neutral complex *trans*-$ICr(CO)_4CMe$[8,9] but slightly bent in the salt *trans*-$[PMe_3Cr(CO)_4CMe]BCl_4$.[8] In seven out of eight chromium complexes containing CPh and $CNEt_2$ ligands the Cr–C–R units are bent, as predicted.[8–15]

The carbynes seem to be stronger π acids than the carbonyl ligand. The comparison is only meaningful when all ligands are treated as equally charged fragments. For example, CMe withdraws 0.84 electron from the metal fragment, whereas CO withdraws only about 0.40 electron. Of the three carbyne ligands studied, $CNEt_2$ is the weakest π acid; its π orbitals contain 0.46 electron, as Table IV shows. The reason for greater back-donation to carbynes than to carbonyls is evident from Figure 1 and the previous discussion of the bonding abilities of the ligands. The π-accepting orbitals of carbynes are essentially nonbonding in the ligands and therefore lower in energy—thus closer to the π-donating orbitals of the metal fragment—than are 2π orbitals of carbonyls, which are strongly antibonding in those ligands. Our conclusions about the relative π-accepting abilities agree with the observed CO stretching frequencies in the infrared spectra of *trans*-$XCr(CO)_4CR$ (X = Br, I; R = Me, Ph)[23] and *trans*-$XCr(CO)_4CNEt_2$ (X = Cl, Br, I).[11] Very strong e-symmetry bands occur at ca. 2048 cm^{-1} in the complexes with R = Me or Ph but at ca. 1994 cm^{-1} in the complexes containing the $CNEt_2^+$ ligand. The weaker the π acidity of the carbyne ligand, the greater the chromium-to-carbonyls back-donation and the lower the C–O stretching frequency. Our findings agree with crystallographic evidence that the Cr–$CNEt_2$ bond order in several compounds is between two and three.[8,11,15,18]

Bromine p_π orbitals are practically filled and localized on that atom. The populations of all σ-type ligand orbitals are lower than 2.00 electrons, which indicates their donating abilities.

***trans*-$XCr(CO)_4CMe$ (X = Cl, Br, I).** The electronic structures of these three complexes are similar, as can be seen in Figure 2 and Tables I, V, and VI. The crystal structures of various *trans*-$XCr(CO)_4CR$ complexes reveal that equatorial CO groups are bent toward the halogen

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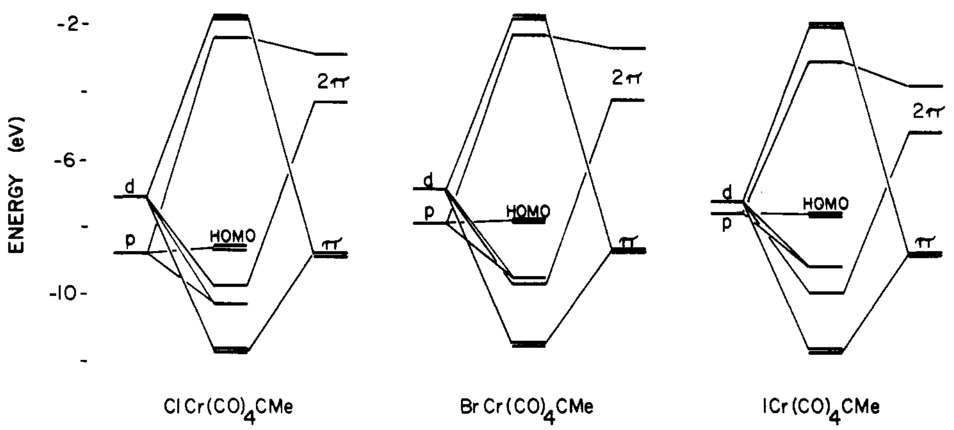

Figure 2. Molecular orbital diagrams for *trans*-XCr(CO)$_4$CMe (X = Cl, Br, I). The fragment orbitals are labeled as in Figure 1, except that p stands for valence p orbitals of the halogens: 3p of Cl, 4p of Br, and 5p of I.

Table VI. Energies and Percent Compositions of Important High-Lying MO's in *trans*-ICr(CO)$_4$CMe

	Cr					CMe	(CO)$_4$	I
ϵ, eV	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	$d_{xz,yz}$	4p	π	2π	5p
−7.57 (HOMO's)[a]								99
−9.17	9				12		11	65
−9.98			56				42	
−11.73[a]				43		37	14	

[a] Doubly degenerate level.

atom.[8] In *trans*-XCr(CO)$_4$CPh (X = Cl, Br), the only compounds for which actual values have been reported, the deviation is about 3°.[10] The effect was ascribed to steric strain induced by the extremely sort axial Cr–C(carbyne) bond.[8] Displacement of equatorial CO groups toward an axial substituent is a very common phenomenon, observed in the crystal and gas-phase structures of numerous octahedral and trigonal-bipyramidal complexes.[24,25] Carbonyls in them are often bent toward the *bulkier* of the two axial ligands, which indicates that the interaction responsible is not primarily steric. It has been concluded from symmetry and perturbation arguments that equatorial carbonyls prefer to bend toward the weaker π acceptor,[26a] or the stronger donor,[26b] which in the carbyne complex is halogen. On the basis of the present calculations, we propose that the likely explanation for the distortion is direct donation from the halogen p_σ orbital into the a_1 combination of 2π orbitals of equatorial carbonyls. A similar carbyne-to-carbonyl donation is weaker. This halogen–carbonyl interaction through space is responsible for the participation of the a_1-symmetry, 2π-derived level of (CO)$_4$ in the Cr–X σ-bonding molecular orbital in every *trans*-XCr(CO)$_4$CR complex, as Tables I–III, V, and VI show. Direct donation has been observed in molecular orbital calculations;[25,27-30] invoked in the interpretation of mass,[25,31] vibrational,[29,32-34] NMR,[35] and NQR spectra;[32] and used to explain chemical reactivity.[33,36] It is conceivable that observed variation of Cr–X bond length as CO groups are replaced by other ligands[8] may be due, at least partly, to changes in the extent of halogen-to-carbonyl direct donation.

Halogen and carbyne ligands are trans to each other in all known complexes that contain them. An exploratory calculation on *cis*-ICr(CO)$_4$CMe leads us to conclude that the overall extent of Cr–ligand π interactions—as represented by the sum of the populations of Cr d_π orbitals, carbyne π-accepting orbitals, and (CO)$_4$ 2π orbitals—is practically the same in the cis and trans isomers. It seems that trans configuration is indeed a result of the mechanism of formation of carbyne complexes from their carbene precursors, as explained by Fischer and his co-workers.[37-39]

In each complex, one of the the two molecular orbitals below the HOMO level corresponds to a Cr–X σ bond and the other molecular orbital represents Cr–(CO)$_4$ π bonding in the equatorial plane. As electronegativity decreases from Cl to Br to I, the halogen p orbital gets destabilized,

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Table VII. Energies and Percent Compositions of Important MO's in *trans*-$PMe_3Cr(CO)_4CMe^+$

	Cr					CMe		$(CO)_4$		PMe_3
ε, eV	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	$d_{xz,yz}$	4p	σ	π	5σ	2π	σ
−5.20 (LUMO's)[a]				31			57		7	
−13.87 (HOMO)			56						42	
−15.41[a]				44			35		15	
−18.19	17				14				6	59
−21.62		39						52		
−21.73	27				9	46		11		

[a] Doubly degenerate level.

causing gradual destabilization of the Cr–X σ bonding molecular orbital from −10.27 to −9.49 to −9.17 eV, respectively. This rise in energy results in an inversion of the two molecular orbitals below the HOMO level in going from the Cl to the I complex. The ordering of these orbitals and other details of the electronic structures can be studied by variable-intensity photoelectron spectroscopy,[40–45] and we would like to encourage such a study.

Other Tetracarbonyl Complexes

The results of calculations on *trans*-$XCr(CO)_4CPh$ (X = Cl, I) and on *trans*-$ICr(CO)_4CNEt_2$ are similar to the results for the corresponding Br complexes. The trend discussed above for the CMe^+ compounds is also evident in the series of three CPh^+ compounds: as the halogen becomes less electronegative, the Cr–X σ-bonding molecular orbital rises in energy from below the Cr–$(CO)_4$ π-bonding orbital in the Cl complex to above that orbital in the I complex.

The cationic complex *trans*-$PMe_3Cr(CO)_4CMe^+$ differs from the compounds discussed so far in that it does not contain halogen. Figure 3 and Table VII show that the π-accepting level of PMe_3 is so high in energy that it does not appreciably interact with d_π orbitals of Cr, so that it stays practically empty (populated by less than 0.05 electron). The calculated atomic charge of P is +0.87. The bonding picture that emerged from the calculation on *trans*-$PMe_3Cr(CO)_4CMe^+$ agrees with conclusions of a crystallographic study of this complex, i.e., chromium-to-phosphorus back-bonding is negligible and the P atom is akin to a phosphonium center.[8]

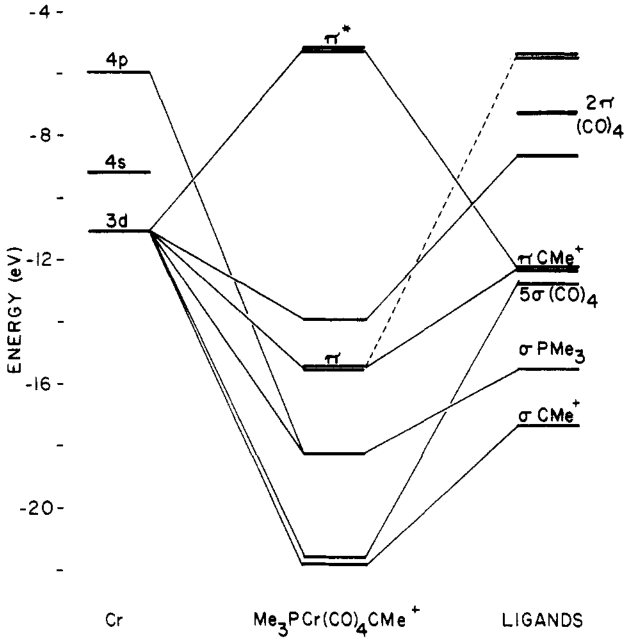

Figure 3. Molecular orbital diagram for *trans*-$PMe_3Cr(CO)_4CMe^+$. The dashed line indicates a minor contribution to the molecular orbital from the fragment orbital.

The three lowest unoccupied molecular orbitals and six highest occupied ones in *mer*-$BrCr(CO)_3(PMe_3)CMe$ are ordered as in *trans*-$ClCr(CO)_4CMe$. The Cr–P σ-bonding molecular orbital lies below the Cr–C(carbyne) π-bonding level. The population of high-energy, π-accepting level in PMe_3 is nearly zero, in accord with experimental findings.[46] A recent study of compounds $(CO)_5CrPR_3$ led to the suggestion that poor π acceptor alkylphosphine may be a weak π donor owing to its e-type level, which corresponds to P-C bonds, below the HOMO.[47] Our calculations on a different compound, *mer*-$BrCr(CO)_3(PMe_3)CMe$, revealed some overlap between this e level of PMe_3 and the d_π orbitals of Cr, but their large energy separation makes the interaction (in terms of overlap populations) practically negligible. In general, interactions between filled π orbitals of ligands and metal d orbitals are not readily detectable by physical methods.[48]

Other substituted halocarbyne complexes have been prepared directly by displacing CO ligands in tetracarbonyl precursors. Two $P(OPh)_3$ ligands in a dicarbonyl complex are trans; all other disubstituted complexes, including the one with two *t*-BuNC groups, contain two ligands of the same kind in cis positions.[37,49] We investigated these preferences by molecular orbital theory.

We carried out calculations on three possible isomers of $BrCr(CO)_2(CNMe)_2CPh$. The bromine and carbyne were trans in all three isomers: one of them contained cis CO ligands, the second had CO groups trans and coplanar with the Ph ring, and the third isomer had trans CO groups and the Ph ring coplanar with the MeNC ligands. We will focus our discussion on π-bonding systems in these three isomers. The changes in configuration of the molecule do not appreciably affect the overall chromium-to-ligand back-donation—the total population of the ligand π-accepting orbitals is practically the same for the three con-

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figurations we studied. This makes sense in molecular orbital terms because various metal–ligand π interactions are not isolated from one another; they participate in an extended π system, which is synergically related to the system of σ bonds. The calculations on different isomers did not reveal any differences in the sequence of filled molecular orbitals; they are ordered as in *trans*-$ICr(CO)_4CMe$. In the trans(CO) isomers, one π-accepting orbital of CPh^+ competes with two carbonyl ligands for the Cr d_π electron density while the other such orbital, orthogonal to the first one, competes with two isocyanide ligands. This causes an energy gap between two Cr–CPh π-bonding molecular orbitals in the trans isomers. This gap is very small in the cis isomer because each π-accepting orbital of CPh^+ competes with one carbonyl and one isocyanide ligand; here nondegeneracy is due solely to nonequivalence of the carbyne orbitals 4π and 5π. The calculations indicate that the observed cis configuration of $BrCr(CO)_2(t\text{-}BuNC)_2CPh$ is probably not due to preferred bonding. The explanation possibly lies in the mechanism of stepwise substitution of two CO groups[37,50] by two RNC ligands, which are stronger σ donors and weaker π acceptors than CO.[20,51] The cis position of two cylindrical RNC ligands probably does not cause appreciable steric strain.

We examined by calculations three possible isomers of $BrCr(CO)_2[P(OH)_3]_2CPh$. In one isomer, the CO groups were cis; in the other two isomers they were trans, the Ph ring being coplanar with CO or with $P(OH)_3$ ligands; Br and CPh^+ were trans in all three configurations. Again, the overall chromium-to-ligand back-donation is practically the same in the three molecules. The phosphite is confirmed to be a weaker π acceptor than the carbonyl.[46,52,53] The diversity of ligands makes the electronic structure of this compound rather complicated. The molecular orbital diagrams for the cis and trans isomers are very similar, and they do not answer the question of orientation in disubstitution. The bulkiness of phosphite ligands can not, by itself, satisfactorily explain their trans position. The cone angle of $P(OPh)_3$ is 128°;[54] PPh_3, whose cone angle is 145°,[54] gives cis-disubstituted complex.[49] The present calculations do not reveal any significant change in bonding as the phenyl ring rotates.

Reactions with Nucleophiles

In our previous article[1] we emphasized the metal–carbyne π-antibonding character and energy isolation of the LUMO's in cationic carbyne complexes—rather than the presumed positive charge at the carbyne carbon atoms[15,39]—as decisive factors responsible for addition of various nucleophiles to these compounds. We corroborate this conclusion now by comparing the results of molecular orbital calculations on *neutral* complexes—*trans*-$XCr(CO)_4CR$—with their chemical behavior. The only such complex reported to undergo nucleophilic addition to its carbyne carbon atom is *trans*-$BrCr(CO)_4CC_6H_4Me$-*p*,[55] the only one whose LUMO corresponds to a Cr–carbyne π antibond (see Figure 1 or 2). In a frontier-controlled reaction at −50 °C, the incoming PMe_3 donates electron density from its HOMO (the phosphorus lone pair) to the LUMO of the substrate; this destroys one Cr–C(carbyne) bond and converts the starting carbyne complex into chromium-substituted phosphorus ylide, akin to carbene complexes.[55]

$$\textit{trans}\text{-}BrCr(CO)_4CR + PMe_3 \rightarrow \textit{trans}\text{-}BrCr(CO)_4C(R)PMe_3$$

Nucleophiles $P(i\text{-}Pr)_3$, PPh_3, $P(OPh)_3$, and *t*-BuNC displace CO ligands in *trans*-$BrCr(CO)_4CPh$ when the reactions are performed between −20 °C and room temperature;[49] PH_3 seems to react similarly.[56] The difference in behavior between PMe_3 on one side and other phosphines and a phosphite on the other was attributed to the difference in nucleophilicity brought about by changing substituents on phosphorus.[39] We believe that experimental conditions, particularly temperature, play an important role in determining the final products of reactions between carbyne complexes and nucleophiles.[1,57] All reported additions of many nucleophiles to various complexes, $CpMn(CO)_2CR^+$ and $ArCr(CO)_2CPh^+$, have been carried out at temperatures about −50 °C or lower, even though these two kinds of compounds are inert to thermal substitution of CO[58] and the carbyne carbon atom is less shielded by a ring (the cone angle of Cp is only about 136°)[54] than by three monodentate ligands.[59] For an addition to occur, the substrate carbyne complex must be sufficiently concentrated in solution; its thermolability necessitates low temperature.[60] Carbene complexes formed by initial nucleophilic attack at carbyne carbon atom can rearrange into substituted carbyne complexes at higher temperatures.[1,57,61] *If this happens, the final products are not indicative of the reaction mechanism.* The influence of temperature upon the outcome of the nucleophilic attack may be studied by attempting reactions between *trans*-$BrCr(CO)_4CC_6H_4Me$-*p* and $P(i\text{-}Pr)_3$, PPh_3, and RNC under the *same* conditions that were used for addition of PMe_3 to this carbyne complex. Our calculations on these three nucleophiles show that the HOMO in every one of them is a σ-type lone pair, localized on the donor atom and isolated energetically from the LUMO and from the next highest occupied molecular orbital. The frontier orbitals of these nucleophiles and of the substrate *trans*-$BrCr(CO)_4CPh$ seem to be well suited for frontier-controlled reactions. Although steric bulkiness of $P(i\text{-}Pr)_3$ and PPh_3 (their cone angles are 160 and 145°, respectively)[54] may hinder addition, we expect that cylindrical molecules of RNC will add relatively easily to the octahedral carbyne complex, as they add to $CpMn(CO)_2CPh^+$.[62]

The calculation on *trans*(PH_3)-$(PH_3)_2(CO)_2FeCPh^+$ shows its LUMO to be an out-of-phase combination containing 17% of the metal fragment orbital π_{xz} and 63% of the carbyne orbital 4π; another 12% is contributed by a higher lying empty orbital of CPh^+, which is more

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localized on the para than on the ortho carbon atoms of the ring. Hence, the LUMO is a metal–carbyne π antibond, largely localized on the ring and isolated in energy from the HOMO and from the next lowest unoccupied molecular orbital. If this is also true about the real osmium compound, the reported addition of nucleophile H^- to the para position of the ring may well be frontier rather than charge controlled.[63]

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Registry No. *trans*-$BrCr(CO)_4CMe$, 51005-78-8; *trans*-$BrCr(CO)_4CPh$, 50701-13-8; *trans*-$BrCr(CO)_4CNEt_2$, 57091-06-2; *trans*-$ClCr(CO)_4CMe$, 62938-49-2; *trans*-$ICr(CO)_4CMe$, 50701-14-9; *trans*-$PMe_3Cr(CO)_4CMe^+$, 54460-85-4; *trans*-$ClCr(CO)_4CPh$, 68851-67-2; *trans*-$ICr(CO)_4CPh$, 50938-50-6; *mer*-$BrCr(CO)_3(PMe_3)CMe$, 52175-60-7; *cis*-$BrCr(CO)_2(CNMe)_2CPh$, 79992-51-1; *trans*-$BrCr(CO)_2(CNMe)_2CPh$, 800-37-5; *cis*-$BrCr(CO)_2[P(OH)_3]_2CPh$, 80028-17-7; *trans*-$BrCr(CO)_2[P(OH)_3]_2CPh$, 80080-80-4; *trans*$(PH_3)-(PH_3)_2(CO)_2FeCPh^+$, 79992-52-2.

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Synthesis and Molecular Structure of $C_5H_5(P\text{-}i\text{-}Pr_3)Pd(\eta^1,\eta^3\text{-}C_3H_4)Pd(P\text{-}i\text{-}Pr_3)Br$: A Compound Formed through Insertion of Allene into a Metal–Metal Bond[1]

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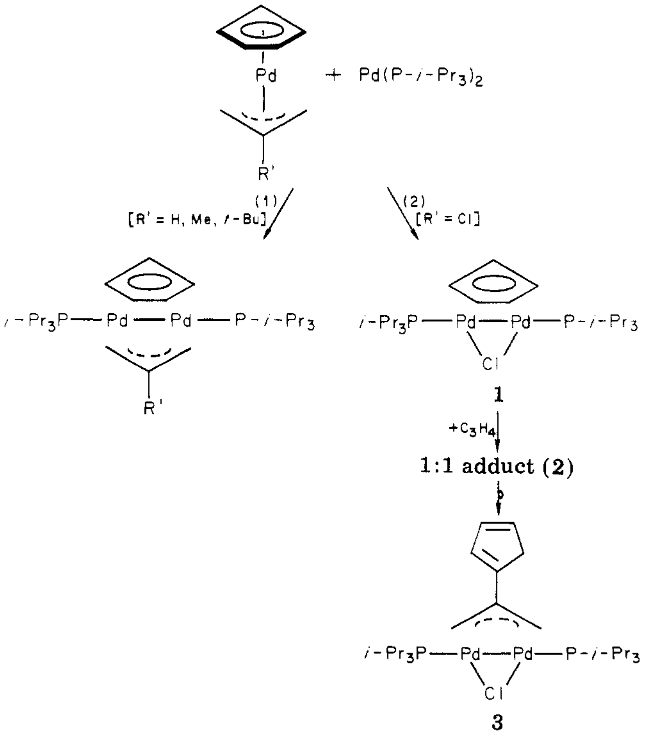
The reaction of $(\mu\text{-}C_5H_5)(\mu\text{-}Br)Pd_2(P\text{-}i\text{-}Pr_3)_2$ (4) with allene leads to a 1:1 adduct $C_5H_5(P\text{-}i\text{-}Pr_3)Pd(\eta^1,\eta^3\text{-}C_3H_4)Pd(P\text{-}i\text{-}Pr_3)Br$ (5) which has been characterized by elemental analysis, mass spectroscopy, NMR spectroscopy, and single-crystal X-ray investigations. The compound crystallizes in the space group $C2/c$ with $a = 25.179$ (9) Å, $b = 17.173$ (8) Å, $c = 16.065$ (9) Å, $\beta = 91.86$ (4)°, and $V = 6943$ (6) Å^3. Full-matrix least-squares refinement gave final discrepancy factors $R_1 = 0.064$ and $R_2 = 0.078$. The molecule contains a bridging allyl group which is (in 2-position) σ bonded to $Pd(P\text{-}i\text{-}Pr_3)(\eta^5\text{-}C_5H_5)$ and π bonded to $Pd(P\text{-}i\text{-}Br_3)Br$. The Pd–Pd distance is 3.58 Å (almost 1 Å longer than in 4) indicating that the formation of 5 from 4 involves a real insertion of allene into the Pd–Pd bond. The structure of the previously described 1:1 adduct prepared from $(\mu\text{-}C_5H_5)(\mu\text{-}Cl)Pd_2(P\text{-}i\text{-}Pr_3)_2$ and allene is shown to be almost identical with that of 5.

There is much current interest in the chemistry of binuclear transition-metal compounds which may serve to activate small molecules such as CO, C_2H_2, C_2H_4, etc.[2] Recently, we have investigated the synthesis and reactivity of a new class of palladium and platinum complexes of the general composition $(\mu\text{-}X)(\mu\text{-}Y)M_2L_2$ in which the bridging ligands X and Y are C_5H_5, $2\text{-}R'C_3H_4$, RCOO, SR, Cl etc. and L is a two-electron donor such as PR_3, $P(OR)_3$, or AsR_3.[3] The most general route for the preparation of these complexes involves the reaction of (X)M(Y) (sometimes only stable as a dimer) with the coordinatively unsaturated compounds ML_2 (e.g., $M(P\text{-}i\text{-}Pr_3)_2$, $M(P\text{-}c\text{-}Hx_3)_2$, etc.) or suitable precursors $(L')ML_2$ where L′, for example, is a substituted olefin.[4]

During our investigations of the synthesis of the complexes $(\mu\text{-}X)(\mu\text{-}Y)Pd_2(P\text{-}i\text{-}Pr_3)_2$ with X = C_5H_5 and Y = $2\text{-}R'C_3H_4$ from $C_5H_5Pd(2\text{-}R'C_3H_4)$ and $Pd(P\text{-}i\text{-}Pr_3)_2$, we observed[5] that for R′ = H, Me, or *t*-Bu the expected product $(C_5H_5)(2\text{-}R'C_3H_4)Pd_2$ $(P\text{-}i\text{-}Pr_3)_2$ is formed (eq 1) whereas for R′ = Cl the corresponding compound 1 containing chloride rather than 2-chloroallyl as the bridging ligand is obtained (eq 2). An alternative route to the complex 1 has been described by Felkin and Turner, who used $C_5H_5Pd(P\text{-}i\text{-}Pr_3)Cl$ and Mg as starting material.[6]



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