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Electronic Spectra and Electronic Structure of Some New Carbon- and Oxygen-Bonded Carbonyl Complexes. $Mo(phen)(P(C_6H_5)_3)_2(COAl(C_2H_5)_3)_2$ and Related Species

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Carbon- and oxygen-bonded carbon monoxide has been achieved for an electron-donor-substituted metal carbonyl, $Mo(phen)(P(C_6H_5)_3)_2(CO)_2$, which interacts with Lewis acids such as $Al(C_2H_5)_3$, $Al(i\text{-}C_4H_9)_3$, and $Ga(CH_3)_3$. Infrared spectra indicate the formation of simple Mo–CO–Al bridges. Adduct formation results in a large blue shift for a charge-transfer band in the molybdenum complex. The influence of methyl substitution (on 1,10-phenthroline) and other lines of evidence indicate the transition is $Mo(CO)_2$ (π_{b_1}) → phen ($\pi^*_{b_1}$) in nature. The change in charge-transfer spectrum upon adduct formation is discussed in terms of a simple molecular orbital treatment, from which it is concluded that addition of a Lewis acid to the oxygen of a carbonyl lowers the energy of the $Mo(CO)_2$ π_{b_1} molecular orbital by increasing Mo–CO back-π-bonding. Shifts in the charge-transfer spectra may be used to infer the following order of electron-pair acceptor strength: $Al(C_2H_5)_3 > Al(i\text{-}C_4H_9)_3 > Ga(CH_3)_3$.

Introduction

The recently discovered phenomenon of carbonyl basicity in metal carbonyls has been demonstrated for bridging carbonyls[1] and terminal carbonyls in carbonyl anions.[2,3] In the present study, we extend this phenomenon to another class of compounds—donor substituted metal carbonyls. The particular compounds chosen for study, 1,10-phenanthroline-substituted $Mo(CO)_6$, display charge-transfer electronic transitions in the visible region. The frequency of these bands is highly sensitive to Lewis acid addition on the carbonyl and provides good insight into the electronic perturbation of a CO ligand by a Lewis acid.

Experimental Section

The aluminum alkyl adducts are highly air sensitive and were handled accordingly. The general procedures have been outlined previously.[1]

Synthesis.—$MoC_3H_5(CH_3CN)_2(CO)_2Br$, prepared as a powdery yellow-orange solid by published procedures,[4] was used in the synthesis of $Mo(CH_3CN)_2(PPh_3)_2(CO)_2$ which is a bright yellow fluffy solid used as the starting material for the phenanthroline derivatives. For both of these compounds, good C, H, and N analyses were obtained. The phenanthroline derivatives $Mo(LL)(P(C_6H_5)_3)_2(CO)_2$, where LL = 1,10-phenanthroline (phen), 5,6-dimethyl-1,10-phenanthroline, 4,7-dimethyl-1,10-phenanthroline, and 3,4,7,8-tetramethyl-1,10-phenanthroline, were prepared using slight modification of the published procedure for the unsubstituted phenanthroline complex.[5] A slurry of $Mo(CH_3CN)_2(PPh_3)_2(CO)_2$ and a slight molar excess of the phenanthroline were stirred together under nitrogen overnight in degassed acetonitrile. The dark solid which settled out was filtered and washed three times each with acetonitrile and anhydrous ether and was dried under vacuum. These compounds were treated as if they were air sensitive; however, no decomposition was noted on brief exposure to air. Analyses were usually good for H and N but slightly low for carbon. *Anal.* Calcd for $Mo(5,6\text{-}dmphen)(PPh_3)_2(CO)_2$: C, 70.59; H, 4.79; N, 3.17. Found: C, 69.71; H, 4.83; N, 3.86. Carbonyl stretching frequencies of $Mo(phen)(PPh_3)_2(CO)_2$, 1800 and 1729 cm^{-1}, fall between those of two published reports: 1805 and 1730 cm^{-1} [5] and 1792 and 1724 cm^{-1}.[6] Carbonyl stretching frequencies were observed for the substituted phenanthroline complexes such as follows: 5,6-dimethylphenanthroline, 1810 (s) and 1725 (s) cm^{-1}; 4,7-dimethylphenanthroline, 1806 (s) and 1726 (s) cm^{-1}; 3,4,7,8-tetramethylphenanthroline 1799 (s), 1726 (s) cm^{-1}.

$Mo(phen)_2(CO)_2$ was prepared by a modification of a published method[7] by refluxing $Mo(CO)_6$ and 1,10-phenanthroline in tetrahydronaphthalene until the solution became fully black. Filtration yielded an air-sensitive, free-flowing black compound which was washed with three portions each of benzene and ethanol, dried under vacuum, and quickly removed to the drybox. Infrared spectra showed very weak bands possibly due to $Mo(phen)(CO)_4$, which were not altered by extracting the sample with ethanol. Excellent analytical results were obtained for C, H, N, and Mo.

$Mo(CO)_6$ (Alfa), which was resublimed, displayed an infrared spectrum agreeing with the literature.[8] B_2H_6, $Zn(CH_3)_2$, and $Ga(CH_3)_3$, which were prepared and characterized in previous work, were distilled on the vacuum line prior to use. SO_2 (Matheson) was used without purification.

$Mo(LL)(PPh_3)_2(COAlR_3)_2$, where LL is 1,10-phenanthroline or 5,6-dimethylphenanthroline and R is ethyl or isobutyl, was prepared in an inert atmosphere by mixing 0.9 mmol of the molybdenum compound with 1.8 mmol of trialkylaluminum in 100 ml of benzene. Reaction was instantaneous with a change in color from deep blue to cherry red. The volume of solvent was reduced under vacuum until crystallization was induced. About 50 ml of degassed heptane was added and the volume was further reduced by vacuum. The very air-sensitive, rust-colored complex was filtered and washed with two 5-ml portions of very dry and air-free heptane and then stored under nitrogen. Infrared spectra of samples selected for analysis showed two carbonyl frequencies of approximately equal intensity, *ca.* 80 cm^{-1} lower energy than parent compound (Table I), and contained no CO bands characteristic of the parent or of a 1:1 adduct, which would require one ν_{CO} at higher energy than the parent compound. *Anal.* Calcd for $Mo(phen)(PPh_3)_2[COAl(C_2H_5)_3]_2$: C, 68.63; H, 6.32; N, 2.58; Al, 4.97. Found: C, 68.30; H, 6.25; N, 2.40; Al, 4.68. Calcd for $Mo(5,6\text{-}dmphen)(PPh_3)_2[COAl(C_2H_5)_3]_2$: C, 69.05; H, 6.52; N, 2.52. Found: C, 69.25; H, 6.85; N, 3.00. $Mo(phen)_2[COAl(C_2H_5)_3]_2$ was prepared in the manner described above to yield a dull black compound. *Anal.* Calcd: C, 61.61; H, 6.26; N, 7.56; Al, 7.29. Found: C, 61.38; H, 6.19; N, 7.50; Al, 7.48.

Spectra.—Visible spectra were obtained on a Cary 14 recording spectrophotometer in benzene solutions using vacuum-tight cells.[9] The sample compartment was thermostated to within 0.1° during runs, and a solvent reference blank was used. Samples were prepared by dissolving a weighed portion of the parent metal carbonyl in dried, air-free solvent, followed by the addition of the Lewis acid. Spectrophotometric titrations were carried out by the addition of successive measured quantities of gaseous Lewis

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[1] (a) N. J. Nelson, N. E. Kime, and D. F. Shriver, *J. Amer. Chem. Soc.*, **91**, 5173 (1969); (b) A. Alich, N. J. Nelson, D. Strope, and D. F. Shriver, *Inorg. Chem.*, **11**, 2976 (1972).

[2] J. C. Kotz and C. D. Turnipseed, *Chem. Commun.*, 41 (1970). Kotz and Turnipseed's system involves a zwitterion.

[3] (a) J. M. Burlitch and R. B. Petersen, *J. Organometal. Chem.*, **24**, C65 (1970); (b) R. B. Petersen, J. J. Stezowski, C. Wan, J. M. Burlitch, and R. E. Hughes, *J. Amer. Chem. Soc.*, **93**, 3532 (1971).

[4] H. T. Dieck and H. Friedel, *J. Organometal. Chem.*, **14**, 375 (1968).

[5] H. T. Dieck and H. Friedel, *Chem. Commun.*, 411 (1969).

[6] C. G. Hull and M. H. B. Stiddard, *J. Chem. Soc. A*, 710 (1968).

[7] H. Behrens and N. Harder, *Chem. Ber.*, **97**, 426 (1964).

[8] G. Bor, *Spectrochim. Acta*, **18**, 817 (1962).

[9] D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969, p 96.

TABLE I

CO AND AlR$_3$ INFRARED BANDS[a]

Lewis base compound	Lewis acid	ν_{CO}, cm^{-1}	$\Delta\nu_{CO}$,[b] cm^{-1}	ν_{AlR_3}, cm^{-1}
Mo(phen)(PPh$_3$)$_2$(CO)$_2$		1729 s		
		1800 s		
	2[Al(C$_2$H$_5$)$_3$]	1633 s	−82	635 s, br
		1731 s		683 m
				1183 w
	2[Al(*i*-C$_4$H$_9$)$_3$]	1633 s	−84	645 m
		1727 s		686 s
				1174 m
Mo(5,6-dmphen)(PPh$_3$)$_2$(CO)$_2$[c]		1725 s		
		1810 s		
	2[Al(C$_2$H$_5$)$_3$]	1627 s	−90	638 m, br
		1727 s		683 w
				1183 ww
Mo(phen)$_2$(CO)$_2$		1732 s		
		1736 s		
		1766 s		
	2[Al(C$_2$H$_5$)$_3$]	1565 s	−121	649 m, br
		1584 s		678 w
		1684 s		1185 w

[a] Spectra were recorded for Nujol mulls. Except for the Al(*i*-C$_4$H$_9$)$_3$ adduct, where analyses were not obtained, the spectra were obtained on analyzed samples (see data in text). [b] Shift in average ν_{CO} upon adduct formation. [c] 5,6-dmphen = 5,6-dimethyl-1,10-phenanthroline.

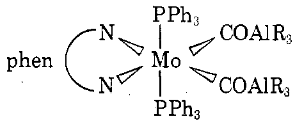
acid on the vacuum line (GaMe$_3$, B$_2$H$_6$, SO$_2$, ZnMe$_2$) or a weighed quantity of a liquid Lewis acid (AlEt$_3$, Al(*i*-Bu)$_3$). A few experiments were also performed in which the adduct was back-titrated by the addition of triethylamine. Infrared spectra were obtained with Beckman IR9 or IR10 instruments on Nujol mulls of the sample. The low solubility of these compounds in suitable solvents prevented solution spectroscopic studies in the infrared region.

Results and Discussion

Al(C$_2$H$_5$)$_3$ and Al(*i*-C$_4$H$_9$)$_3$ Adducts.—In contrast with all previously reported –CO– bridged adducts of mononuclear carbonyl derivatives, the new complex Mo(phen)(PPh$_3$)$_2$(COAlEt$_3$)$_2$ and its analogs involve more than one basic carbonyl. Apparently these neutral molybdenum hexacarbonyl derivatives are even more basic than (h^5-C$_5$H$_5$)Mo(CO)$_3^-$ and its analogs all of which have higher weighted average CO stretching frequencies than the neutral phenanthroline compounds. This observation agrees with previous correlation of high basicity with low ν_{CO}; however the comparison is not definitive because of differences in the reaction conditions. To obtain a clearer comparison of ν_{CO} and basicity, the reaction of triethylaluminum with Mo(CO)$_6$ was investigated since this carbonyl has a weighted average ν_{CO} 276 cm^{-1} higher than Mo(phen)(PPh$_3$)$_2$(CO)$_2$. For a methylcyclohexane solution 2 × 10^{-3} *M* in Mo(CO)$_6$ and 0.070 *M* in Al$_2$Et$_6$ no significant alteration of the CO stretching frequencies of Mo(CO)$_6$ was observed, clearly demonstrating that the donor-substituted compounds, which have low ν_{CO}, are much more basic than the parent molybdenum hexacarbonyl.

Another difference from most previously studied carbonyl bases[1-3] is the lack of cyclopentadienyl groups in the molybdenum complexes studied here.[10] It appears that only very stable carbonyl derivatives are sufficiently resistant to attack by aluminum alkyls and aryls to form simple adducts. In line with this idea we have obtained evidence that the Lewis acid nmr shift reagent Eu(fod)$_3$, which is known to interact with basic carbonyls,[11] is less destructive than trialkylaluminum.[12]

Formulation of the new compounds as simple carbonyl adducts is substantiated by the characteristic decrease in ν_{CO} upon adduct formation, and the facile regeneration of the parent complex by bases such as triethylamine or by air. From the observation of two CO stretching frequencies (indicating a cis arrangement of carbonyls) and from steric considerations the probable structure of the adduct is I.



I

Incremental addition of AlEt$_3$ or back-titration with NEt$_3$ indicates that adduct formation proceeds in a stepwise fashion with the 1:1 AlEt$_3$ adduct having a visible absorption maximum around 530 nm. While a solid trimethylgallium adduct was not isolated, incremental addition of GaMe$_3$ to a benzene solution of Mo(phen)(PPh$_3$)$_2$(CO)$_2$ produced one set of isosbestic points, Figure 1, indicating a single adduct of 1:1 stoichiometry. Data on the solution spectra of the various phenanthroline complexes and their adducts are collected in Table II and analyzed in detail in the following two sections.

Judging from visible spectroscopy, ZnMe$_2$, SO$_2$, and B$_2$H$_6$ fail to interact with Mo(phen)(PPh$_3$)$_2$(CO)$_2$, while vanadyl(IV) bis(acetylacetonate) causes immediate decomposition.

Assignment of the Electronic Spectrum.—Of particular interest is the dramatic color change from intense blue-green of the parent to deep red of the trialkylaluminum adduct. The color of the parent Mo(phen)(P(C$_6$H$_5$)$_3$)$_2$(CO)$_2$ primarily arises from a broad absorption centered around 693 nm (14.4 kK) with a molar absorptivity of 7.7 × 10^3 mol^{-1} cm^{-1} l. When the compound contains two acetonitrile ligands in place

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(10) Two reports of –CO– bridged compounds not containing cyclopentadienyl groups are as follows: E. L. Brown and D. B. Brown, *Chem. Commun.*, 67 (1971); J. Chatt, J. R. Dilworth, G. J. Leigh, and R. L. Richards, *ibid.*, 959 (1970). In the former report, the carbonyl ligand is forced into a bridging environment by the presence of CN ligands.

(11) T. J. Marks, J. Kristoff, A. Alich, and D. F. Shriver, *J. Organometal. Chem.*, **33**, C35 (1971).

(12) D. Strope, unpublished observations, Northwestern University, 1971.

TABLE II

VISIBLE AND NEAR-ULTRAVIOLET BANDS FOR LEWIS ACID ADDUCTS OF $Mo(phen)(PPh_3)_2(CO)_2$ AND RELATED COMPOUNDS IN BENZENE SOLUTION

Lewis base	Concn, *M*	Lewis acid	Concn, *M*	λ_{max}, nm	ν_{max}, cm^{-1}	M^{-1}, cm^{-1}
$Mo(phen)(PPh_3)_2(CO)_2$	1.23×10^{-4}			693	14,400	7,690
				396	25,300	15,950
		$Al(C_2H_5)_3$	2.3×10^{-1}	499	20,000	4,320
				442	23,700	3,510
		$Al(i\text{-}C_4H_9)_3$	3.66×10^{-2}	514	19,500	4,520
				416	24,100	3,400
	8.15×10^{-4}	$Ga(CH_3)_3$	1.45×10^{-1}	623	16,100	>6,860
				346	28,900	>14,100
$Mo(5,6\text{-dmphen})(PPh_3)_2(CO)_2$	1.30×10^{-4}			691	14,500	7,660
				397	25,200	15,500
		$Al(C_2H_5)_3$	5.76×10^{-2}	502	19,900	4,550
				422	23,700	3,590
	1.08×10^{-4}	$Al(i\text{-}C_4H_9)_3$	1.38×10^{-1}	511	19,600	4,610
				417	24,000	3,400
$Mo(phen)_2(CO)_3$[a]	$<2 \times 10^{-4}$			730	13,700	
				610	16,800	
				460	21,700 w, sh	
				381	26,300	
		$Al(C_2H_5)_3$		500–550	18,200–20,000	
				422	23,700	

[a] Compound dissolves very slowly with decomposition.

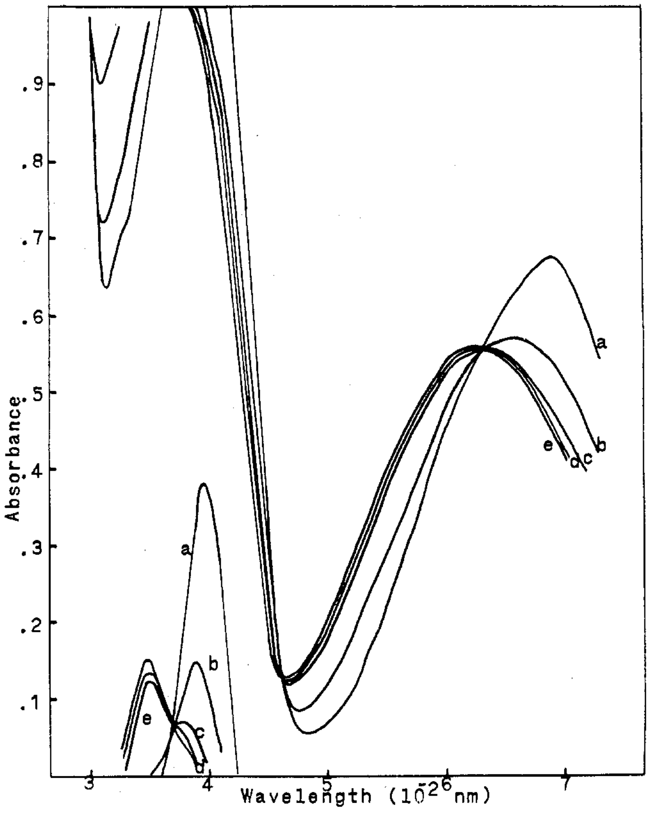

Figure 1.—Electronic spectrum of $Mo(phen)(PPh_3)_2(CO)_2$ (8.2×10^{-5} *M*) in the presence of $GaMe_3$. $GaMe_3$ concentrations: a, 0.0; b, 2.8×10^{-2}; c, 5.5×10^{-2}; d, 9.3×10^{-2}; e, 1.5×10^{-1} *M*.

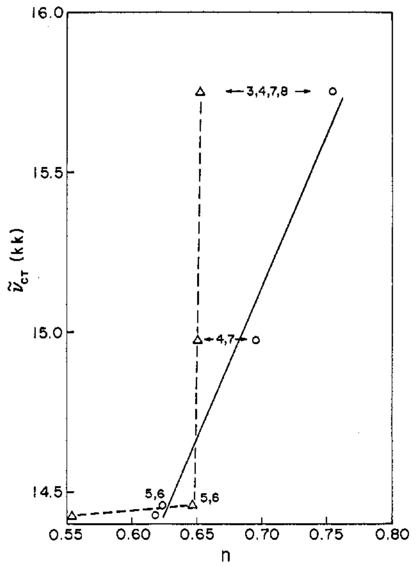

Figure 2.—Charge-transfer transition energy of $Mo(LL)(PPh_3)_2(CO)_2$ *vs.* HMO π^* energy of LL where LL = 1,10-phenanthroline and its methyl derivatives: O, lowest unoccupied b_1 orbital; Δ, lowest unoccupied a_2 orbital. If methyl substituents are present, their positions are indicated by numbers associated with the points.

of 1,10-phenathroline, this band is missing and no intense features are observed below 33 kK. The intensity and specific occurrence with the aromatic diimine ligand indicate charge-transfer transition involving the 1,10-phenanthroline. Presence of the zero oxidation state d^6 central Mo atom in these complexes leaves little doubt that the sense of the charge transfer is Mo (d) → phen (π^*). A similar assignment has previously been demonstrated for the long-wavelength absorption in $Mo(phen)(CO)_4$.[13] More precise assignments are possible from a consideration of the spectral influence of methyl substituents.

In its simplest form, charge-transfer theory leads to the prediction that the transition energy, E_{CT}, should be linearly related to the electron affinity of the acceptor orbital, *A* (which we equate with the energy of a π^* phenanthroline orbital) by $E_{CT} = I + A - Q$, where *I* is the ionization potential of the donor orbital and *Q* is the coulombic stabilization of the excited state. While the detailed theory, to be discussed later, leads to a more involved expression, a monotonic relation is still expected between E_{CT} and the energy of the π^* orbital, where the relevant energies may be calculated using Hückel theory and a heteroatom model for the

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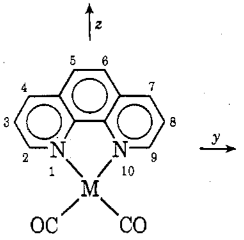
[13] H. Saito, J. Fugita, and K. Saito, *Bull. Chem. Soc. Jap.*, **41**, 359, 863 (1968).

methyl group with $h(\mathrm{N}) = 0.5$, $h(\mathrm{CH_3}) = 2.0$, $h(\mathrm{C}_\alpha) = -0.16$, $k(\mathrm{CN}) = 1.0$, and $k(\mathrm{C{-}CH_3}) = 0.77$.[14] As shown in Figure 2, a smooth correlation is observed between E_{CT} and the calculated lowest empty b_1 MO energy of the various methylphenanthroline complexes. The figure also demonstrates a lack of correlation for the lowest a_2 π^* orbital. From these comparisons we conclude that the acceptor π^* orbital on phen has b_1 symmetry. Significant intensity is expected only for the transition occurring in the direction of charge transfer (z in II).[14] Therefore the group theory leads



II

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to an ${}^1A_1 \rightarrow {}^1A_1$ assignment for the transition which is only compatible with electron transfer from a b_1 donor orbital. Since large metal–carbonyl $d(\pi)$–$p(\pi)$ interaction is expected, the donor level for the CT is best represented as a filled b_1 π-type MO of the Mo(CO)$_2$ portion. For purposes of the following discussion, this molecular orbital is constructed from a linear combination of Mo d_{xz}, carbonyl C p_x and carbonyl O p_x.

Electronic Structure.—Because of the low symmetry of Mo(phen)(PPh$_3$)$_2$(CO)$_2$ we were not encouraged to attempt a complete semiempirical calculation. Instead a parametrized model is constructed, in the spirit of charge-transfer complex theory, from two fragments of the complex, 1,10-phenenthroline and Mo(CO)$_2$, which represent the donor and acceptor, respectively. Fortunately, reasonable molecular orbital calculations may be performed for these fragments individually. For the acceptor phen π^* orbital we employ the HMO results cited above where the Hückel parameters are available from a previous detailed fit to experimental data.[14] Similarly, the donor b_1 π MO of Mo(CO)$_2$ is calculated by using matrix elements (H_{OO}, H_{CC}, H_{MoMo}, H_{CO}, and corresponding S elements) from the self-consistent configuration and charge calculations of Brown and Rawlinson, which reproduce well the ground-state properties of Mo(CO)$_6$.[15] (S_{MoC} was transformed into our coordinate system, H_{MoC} was calculated using Cusachs' approximation,[15,16] and C–C interactions were included.) The resulting 5 × 5 secular determinant, $|H_{ij} - S_{ij}E| = 0$, was solved by standard methods to yield the energies and wave functions. Designating the highest filled π MO of Mo(CO)$_2$ as ϕ_2 (this orbital has b_1 symmetry) and the vacant b_1 π^* orbital on phen as ϕ_1, we approximate the molecular orbitals of the complex by a linear combination of component molecular orbitals

$$\begin{aligned} \psi_1 &= C_1\phi_1 + C_2\phi_2 \\ \psi_1 &= C_2\phi_1 - C_1\phi_2 \end{aligned} \tag{1}$$

With neglect of overlap, the variational treatment yields a 2 × 2 secular determinant, from which the transition energy between the two levels may be calculated (eq 2). H_{11} is the previously calculated energy

$$E_{\mathrm{CT}} = \sqrt{H_{11}^2 + H_{22}^2 - 2H_{11}H_{22} + 4H_{12}^2} \tag{2}$$

of the phen b_1 π^* MO, and H_{22} is the calculated energy of the highest filled b_1 π orbital on Mo(CO)$_2$. If only nearest neighbor interactions are included, the element $H_{12} = \langle\phi_1|\mathcal{H}|\phi_2\rangle$ takes the value $2C_{2\mathrm{N}}C_{1\mathrm{Mo}}H_{\mathrm{NMo}}$, where $C_{2\mathrm{N}}$ is the coefficient of the p_x orbital for one of the nitrogens in ϕ_2 and $C_{1\mathrm{Mo}}$ is the coefficient of the Mo d_{xz} orbital in ϕ_1. A range of H_{NMo} values was explored bracketing that obtained using Cusachs' approximation for which $H_{\mathrm{NMo}} = 17.4$ kK. The results are not highly sensitive to the exact value chosen for H_{NMo}.

A scaling problem arises for H_{11} and H_{22} because the former energy is calculated in units of the C–C resonance integral (β) with the zero in energy equal to the carbon coulomb integral, while H_{22} is referenced to valence-orbital ionization potentials.[15,17] This problem is further complicated by the influence of methyl substitution on the basicity of the phenanthroline nitrogens, which results in energy shifts for the metal-containing portion of a complex.[14] To circumvent these complications we define H_{11} and H_{22} as shown in eq 3 and 4. The unit of energy used here is the kilokaiser, 1000 cm^{-1} (8.066 kK = 1 eV), and n is the conventional

$$H_{11} = n\beta + c \tag{3}$$

$$H_{22} = (10.31 + E_3)8.066\ \mathrm{kK} \tag{4}$$

Hückel energy in units of the C–C resonance integral β. The value chosen for β, -21 kK (-2.6 eV), fits many correlations between Hückel calculations and observed energies.[18] The value of c is calculated from E_{CT} for the parent Mo(LL)(PPh$_3$)$_2$(CO)$_2$ so that the zero in energy corresponds to that of the highest filled π molecular orbital energy, E_3, of the Mo(CO)$_2$ moiety. Accordingly, when E_3 assumes the value -10.31 eV, calculated for Mo(CO)$_2$ in the absence of Lewis acid, eq 4 yields a value of zero for H_{22}. To compensate for the previously mentioned methyl inductive effects, c is calculated separately for each of the methylphenanthroline complexes. As shown in Table III, the

TABLE III

ENERGY PARAMETER, c, AND CHARGE-TRANSFER ENERGY FOR Mo(LL)(PPh$_3$)$_2$(CO)$_2$ AND ITS Al(i-Bu)$_3$ ADDUCT

		1:2 adduct with Al(i-Bu)$_3$ E_{CT}, kK	
LL	c, kK	Obsd	Calcd
1,10-Phenanthroline	−2.59	19.50[a]	
5,6-Dimethyl-1,10-phenanthroline	−2.61	19.57	19.60
4,7-Dimethyl-1,10-phenanthroline	−2.82	19.96	20.80
3,4,7,8-Tetramethyl-1,10-phenanthroline	−3.82	20.75	20.35

[a] The observed E_{CT} for the phen complex was used to establish the change in H_{OO} upon adduct formation; E_{CT} for all other adducts were calculated using this value of H_{OO}. The Mo–N resonance integral $H_{\mathrm{NMo}} = 17.4$ kK was calculated by Cusachs' approximation.

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(14) P. Day and N. Sanders, *J. Chem. Soc. A*, 1530, 1536 (1967).

(15) D. A. Brown and R. M. Rawlinson, *J. Chem. Soc. A*, 1530 (1969). A similar calculation for Mo(CO)$_6$ is given by N. A. Beach and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 5713 (1968).

(16) L. C. Cusachs, *J. Chem. Phys.*, **43**, 5157 (1965).

(17) H. Basch, A. Viste, and H. B. Gray, *Theor. Chim. Acta*, **3**, 458 (1965).

(18) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.

value of c does not vary greatly from one complex to the next. Coordination of the carbonyl oxygen to an acceptor results in a removal of negative charge from oxygen and an increase in the oxygen valence orbital ionization potential, H_{OO}.[19] A graph of calculated E_{CT} (eq 2) *vs.* H_{OO} reveals that the latter quantity should be -24.40 eV to fit the spectrum of Mo(phen)$(PPh_3)_2(COAlEt_3)_2$ and this value of H_{OO} may be employed along wtih the known variation of valence-orbital ionization potentials with charge[17] to yield $+0.085$ e for the charge shifted from oxygen to aluminum upon adduct formation, Δq_O. The exact value of Δq_O cannot be taken literally, but the magnitude is reasonable and thus supports the reasonableness of the model.

One of the best checks of the model comes from a comparison of the calculated and observed values for the charge-transfer energy of the 1:1 adduct Mo(phen)$(PPh_3)_2(CO)(COAlEt_3)$. A calculated value is obtained by setting H_{OO} for one oxygen at the perturbed value of -24.40 eV and the other at the unperturbed value of -15.70 eV in the molecular orbital calculation for $Mo(CO)(COAlEt_3)$. The resulting E_3 is employed in eq 4 to give H_{22}, which upon substitution into eq 2 yields a charge-transfer energy of 19.3 kK (518 nm). This compares favorably with the value determined experimentally, 530 ± 10 nm. Significantly, both theory and experiment show a much larger shift in E_{CT} upon addition of the first triethylaluminum than upon addition of the second. Another less stringent test is afforded by comparison of calculated and observed shifts in E_{CT} for the various methylphenanthroline complexes, Table III. The general picture which emerges from the spectral interpretation is that addition of a Lewis acid to the oxygen of a carbon monoxide ligand greatly increases back-π-bonding to CO.

A particularly interesting comparison can be made between the Δq_O values determined from the CT spectra for triethylaluminum, triisobutylaluminum, and trimethylgallium complexes. As described previously, Δq_O for $AlEt_3$ is $+0.085$, for $Al(i\text{-}Bu)_3$ it is $+0.080$, and for $GaMe_3$ it is $+0.035$ atomic charge unit. This order is in harmony with the chemistry of these acids which suggests that $AlEt_3$ forms the strongest donor–acceptor bonds and $GaMe_3$ the weakest in this series.[20]

Conclusion

The spectra of $Mo(LL)(PPh_3)_2(CO)_2$ complexes and their adducts are successfully described by a simple molecular orbital model in which the transition of interest arises from a b_1 symmetry MO which is mainly localized on $Mo(CO)_2$ (ϕ_2), to a b_1 symmetry MO which is mainly 1,10-phenanthroline π^* in character (ϕ_1). Because absolute energies are not easily obtainable for ϕ_2 and ϕ_1, the degree of mixing (eq 1) of ϕ_2 and ϕ_1 in the ground and excited states cannot be assessed accurately. However, qualitative (and semiquantitative) success of the treatment is insensitive to the degree of mixing. The influence of a Lewis acid on the complex is introduced *via* a perturbation of the coulomb integral, H_{OO}, of the oxygen to which the acid is attached. The effect of this perturbation is to lower the energy of the $Mo(CO)_2$ donor orbital, ϕ_2, and thus increase the energy of the charge-transfer transition. The influence which the added Lewis acid has on the donor $Mo(CO)_2$ energy level through changes in the σ donation of CO toward Mo was not included in our model, but it can be anticipated from the weak σ-donor character of CO that σ effects are less important than changes in π bonding which are the basis of the present model. With cyanide compounds where C–metal σ bonding is larger, it is necessary to include both σ and π perturbations by the added Lewis acid to understand the available spectral data.[21]

A somewhat different perspective is provided by a simple expression (5), resulting from perturbation theory, where ΔE_{CT} is the change in energy of the charge-

$$\Delta E_{CT} \simeq (\Delta \rho_0)(\Delta H_{OO}) \qquad (5)$$

transfer transition upon adduct formation, $\Delta \rho_0$ is the change in charge density on the oxygen atom between the ground and excited states of the parent complex, and ΔH_{OO} is the change in coulomb integral o-oxygen arising from the attachment of a Lewis acidf It may be seen from this equation that the *order* of electron-pair acceptor strengths for various Lewis acids attached to oxygen should be directly related to ΔE_{CT}.

The present work provides another example of the connection between low ν_{CO} and basicity of the carbonyl ligands. This correlation is very useful as a guide to those metal carbonyls which may display basicity, and it also provides a good illustration of the long-held idea that a low ν_{CO} corresponds to high electron density on the carbonyl. As with any spectral criterion for reactivity, it can be anticipated that the correlation will fail when steric and other more subtle factors become influential.

The coordinated carbonyl oxygen is found to interact with Al(III),[1-3] Ga(III), and Eu(III),[11,22] all of which are hard acids. By contrast, the soft acid BH_3 failed to interact with the carbonyl oxygens of Mo(phen)$(PPh_3)_2(CO)_2$. We conclude that the oxygen end of the coordinated CO ligand is hard. The contrast between the soft π-acceptor carbon and hard (but weak) σ-donor oxygen of carbon monoxide readily explains the lack of $M—C{\equiv}O—M$ bridges among the conventional metal carbonyl compounds since these compounds involve soft electron-rich metals in low oxidation states. Conceivably an example can be found in which coordination at oxygen is attained by a transition metal in a high oxidation state. To avoid the complication of a redox reaction, the high-oxidation-state oxygen-coordinated metal would logically come from the left of the transition series.[23]

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[19] This type of perturbation treatment was used with molecular complexes by T. B. Eames and B. M. Hoffman, *J. Amer. Chem. Soc.*, **93**, 3141 (1971), and a similar treatment is successfully employed in describing substituent effects in organic chemistry.[18]

[20] For example the $AlEt_3$ and $Al(i\text{-}Bu)_3$ adducts formed in this study appear to be of comparable stability even though $AlEt_3$ is more highly dimerized. That the $GaMe_3$ compound is the weakest is shown by its tendency to form only a 1:1 adduct at room temperature. The order of electron-pair acceptor strengths usually parallels observed acidities (*e.g.*, ref 21); however, in principle such a parallel need not hold.

[21] D. F. Shriver and J. Posner, *J. Amer. Chem. Soc.*, **88**, 1672 (1966).

[22] A. A. Crease and P. Legzdins, *J. Chem. Soc., Chem. Commun.*, 268 (1972).

[23] Carbon and oxygen coordination to transition metals has been achieved in a different manner by E. L. Brown and D. B. Brown, who incorporated $Fe(CO)(CN)_5^{2-}$ into a Prussian Blue type structure thus forcing CO into a bridging environment between Fe and Co.[10]

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Crystal and Molecular Structures of Di-μ-oxo-bis(diacetylacetonatotitanium(IV))-Bisdioxane, $(TiO(C_5H_7O_2)_2)_2\cdot 2C_4H_8O_2$, and Di-$\mu$-oxo-bis(diacetylacetonatotitanium(IV)), $(TiO(C_5H_7O_2)_2)_2$

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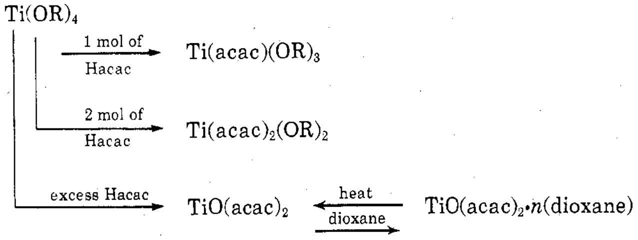
The structures of two crystals of di-μ-oxo-bis(diacetylacetonatotitanium(IV)), $(TiO(C_5H_7O_2)_2)_2$, have been determined by X-ray single-crystal methods, using data collected by counter methods. Crystal I, crystallizing with 2 molecules of dioxane, belonged to space group $P\bar{1}$, a = 12.08 (2) Å, b = 12.81 (1) Å, c = 9.98 (2) Å, α = 123.3 (1)°, β = 96.3 (1)°, γ = 124.0 (1)°, and Z = 1 for the Delaunay-reduced cell. Crystal II, with no molecules of solvent, belonged to space group $P2_1/c$, a = 9.270 (3) Å, b = 14.019 (3) Å, c = 9.644 (3) Å, β = 105.14 (2)°, and Z = 2. Crystal I refined to an R of 9.7% for 963 observed reflections while crystal II refined to an R of 5.0% for 1549 observed reflections. The structures consisted of a cyclic dimer with the titanium atom linked through oxygen atoms. The di-μ-oxo-dititanium ring is planar and slightly distorted from a square, with angles at oxygen being 97° and at titanium 83°. The acetylacetonate rings are very nearly planar. Some bond distances in the acetylacetone ring are C–O, 1.27 (1) Å; C–CH, 1.38 (1) Å; and C–CH_3, 1.52 (1) Å. The octahedral coordination around titanium is somewhat distorted; angles expected to be 90° vary from 83 to 100° while those expected to be 180° differ from this by as much as 20°. The solvent in crystal I is very loosely bound with little or no chemical bonding and is located in approximately spherically shaped holes between dimer units. The dioxane molecules in these sites show considerable disorder.

Introduction

The reaction of titanium alkoxides with acetylacetone and acetoacetate has been studied by Yamamoto and Kambara[1] and Puri, Pande, and Mehrotra.[2] Several products were reported by Mehrotra, *et al.*, depending on the quantity of acetylacetone used.



Yamamoto and Kambara prepared $TiO(acac)_2$ by hydrolysis of $Ti(acac)_2(OR)_2$[1] and proposed a cyclic dimeric structure based on molecular weight measurements and the ir spectrum.

The structure of at least one Ti(IV)–acetylacetonato complex has been studied by X-ray analysis.[3] Hollaway and Bradley[4] studied in detail the nmr spectra as well as some other aspects of metal complexes containing acetylacetone and discussed various factors influencing metal ligand interaction as well as the effects on the acetylacetone group of various ligands coordinated to the metal.

We report here the structure of $\{TiO(acac)_2\}_2$. Two crystals were studied, one containing no solvent and the other crystallizing with two molecules of dioxane; the dioxane shows no chemical bonding to the $\{TiO(acac)_2\}_2$.

Experimental Section

Preparation of this compound followed the procedure of Mehrotra, *et al.*[2] An excess of acetylactone was added to a solution of $Ti(OC_4H_7)_4$ in benzene. After refluxing for several hours, dioxane was added to the mixture and excess solvent distilled. Upon standing, brown crystals formed from the remaining mixture. These were the crystals containing dioxane, *i.e.*, $\{TiO(acac)_2\}\cdot 2C_4H_8O_2$, crystal I. This material was also recrystallized from a mixture of benzene and pyridine, producing crystal II, $(TiO(acac)_2)_2$. Experimental densities were not taken on either crystal due to the instability and solubility in organic solvents.

Crystal I: $(TiO(acac)_2)_2\cdot 2C_4H_8O_2$.—These crystals were stable in equilibrium with the solution from which they were crystallized but lost their crystallinity upon removal from solution, a fact also noted by Yamamoto, *et al.*[1] The crystal used for collection of X-ray data, approximately 0.2 × 0.4 × 1.0 mm, was sealed in a Lindemann glass capillary along with a drop of solvent, and was stable throughout the data collection.

Preliminary Weissenberg photographs indicated a triclinic space group. Lattice parameters shown in Table I were determined on a GE XRD-5 diffractometer by least-squares refinement of 16 independent 2θ measurements using Mo Kα radiation. All intensities below a 2θ of 45° were measured by counting peak intensities for a fixed time, peaking up each reflection before the measurement. Poor quality of the crystal and slight movement in the capillary resulted in relatively unprecise measurements, precluding the inherently better accuracy of the θ–2θ method. The background was estimated as a function of 2θ over the whole range and an average background count for each 2θ was subtracted from the total peak count. Of the 1871 reflections

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