TABLE I

FRIEDEL–CRAFTS PHENYLATION OF $P_3N_3Cl_6$[a]

Expt. no.	$AlCl_3$, moles[e]	Al, g.-atoms[e,f]	$(C_2H_5)_3N$, moles[e]	Yield, %			
				$P_3N_3Cl_6$[g]	$P_3N_3Cl_4(C_6H_5)_2$	$P_3N_3Cl_2(C_6H_5)_4$	$P_3N_3(C_6H_5)_6$
1	4.00			36.7	29.2	(0.3)	
2	2.54			39.9	32.9	(0.4)	
3[b]	2.54			17.3	59.4	4.9	
4[c]	2.54				30.2	24.2	
5	2.54	0.49		7.8	52.8	9.5	
6[d]	2.54	1.29			5.9	31.5	(0.6)
7	6.75		2.00	12.5	69.6	1.3	
8	7.64		3.00	12.8	76.5	2.2	
9	7.64		3.00 (pyridine)	8.4	74.8	2.1	
10	7.64	0.72	3.00		1.6	32.0	0.8

[a] The product yields were calculated with the assumption that all the $P_3N_3Cl_6$ reacted. Unless otherwise mentioned, 48-hr. reaction time. [b] The reaction repeated twice (48-hr. each time). [c] The reaction repeated three times (40, 40, and 30 hr., respectively). [d] 96-hr. reaction time. [e] Per mole of $P_3N_3Cl_6$ (0.100 mole of $P_3N_3Cl_6$ was used in each run). [f] Unrecovered aluminum, 1.85 g.-atoms added initially. [g] Recovered starting material.

The yields given in Table I are based on the amount of product obtained with reasonable purity after recrystallization. Small yields (given in parentheses in the table) were calculated for the crude product obtained from the chromatographic fractions.

Preparation of 2,2,4,4-Tetrachloro-6,6-diphenylcyclotriphosphazatriene (No. 8 of Table I).—Triethylamine (30.4 g., 0.300 mole) was added carefully to a mixture of aluminum chloride (102 g., 0.764 mole) and benzene (150 ml.), and the mixture was refluxed for about 30 min. Solid hexachlorocyclotriphosphazatriene (34.8 g., 0.100 mole; m.p. 112–114°) was added, and the mixture was refluxed (83°) with stirring for 48 hr. The resulting homogeneous solution was poured onto a mixture of ice and concentrated hydrochloric acid (100 ml.), more benzene was added to the mixture, and the benzene layer was separated. The aqueous layer was extracted once with benzene. The combined benzene extracts were washed with water and dried with calcium chloride, and the solvent was removed (rotary film evaporator). The resulting syrup, containing a small amount of benzene, deposited 10.60 g. (0.0246 mole, 24.6%) of fairly pure (m.p. 93.5–96°) 2,2,4,4-tetrachloro-6,6-diphenylcyclotriphosphazatriene, which was collected by filtration and washing with hexane. From this syrup, approximately 25 g. (58%) of the diphenyl compound was found to be isolable in purity of m.p. 93–95.5° by careful crystallization (from a minimum amount of benzene) followed by filtration and washing with ethanol. In this particular run the remaining material was dissolved in hot hexane (100 ml.) and poured into a column packed with acid-washed alumina (370 g.) in hexane. A compressed air pressure was carefully applied to lower the level of the hexane solution to the upper level of the alumina quickly, the pressure was released, more hexane (cold) was added, and elution was continued. After the unchanged starting material (4.43 g., 12.8%) had been eluted, the solvent was changed to 3:7 benzene–hexane to elute the tetrachlorodiphenyl compound. When this compound had been eluted, 2,2-dichloro-4,4,6,6-tetraphenylcyclotriphosphazatriene was eluted quickly with benzene. The yield of 2,2,4,4-tetrachloro-6,6-diphenylcyclotriphosphazatriene was 22.36 g. (0.0519 mole, 51.9%; mostly m.p. 94–95.5°) after recrystallization from hexane, increasing the total yield to 76.5%, and that of 2,2-dichloro-4,4,6,6-tetraphenylcyclotriphosphazatriene was 1.13 g. (0.0033 mole, 2.2%; mostly m.p. 141.5–143°) after recrystallization from benzene–hexane.

Correspondence

The π-Accepting Ability of CO in the Group VI-B Metal Carbonyls

Sir:

Semiquantitative estimates of differences among CO (and MC) bond orders for the group VI-B metal carbonyls and their simple substitution products [$M(CO)_{6-x}D_x$; M = Cr, Mo, W] have recently been made on the basis of the essentially linear relationship between force constants and bond orders for simple molecules containing C–O bonds[1,2] and the assumed applicability of this relationship to metal carbonyl derivatives. The force constants employed were determined through use of the secular equations of Cotton and Kraihanzel.[1,3] In this treatment it was necessary to the determination of "absolute"[4] bond orders to assume a value for the π-accepting ability of CO in $M(CO)_6$. It was therefore proposed[1] that in $M(CO)_6$ the six available (t_{2g}) metallic dπ electrons "tend to be fully used," that the six CO's thus each received one dπ electron (0.5 electron pair), and that the CO bond order in $M(CO)_6$ is thus 0.5 less than in free CO. An extension of this argument leads to the accurate prediction of the observed 0.5 drop in CO bond order from $Mo(CO)_6$ to $Mo(CO)_3$(dien),[5] and this agreement has been taken as a demonstration of the essential correctness of the proposal cited. The evidence given below supports a considerably smaller (*ca.* 0.2 electron pair) π-accepting ability for CO in $M(CO)_6$, and thus correspondingly

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(1) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

(2) F. A. Cotton and R. M. Wing, *ibid.*, **4**, 314 (1965).

(3) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

(4) "Absolute" in the sense that approximate numerical values may be assigned as bond orders for particular M–C and C–O bonds. The M–C and C–O bond orders neglecting d$\pi \rightarrow \pi^*_{CO}$ back bonding were assumed to be 1 and 3; the probable bond orders in CO and CO^+ have been estimated by Moffitt [*Proc. Roy. Soc.* (London), **A196**, 524 (1949)] to be 2.55 and 2.84. See discussion below.

(5) dien = diethylenetriamine.

higher CO bond orders in the parent carbonyls and their simple derivatives.

Gray and Beach[6,7] have given the order of instability of combining π-orbitals for $M(CO)_6$ as $nd\pi < \pi^*CO$, and therefore the relevant occupied π-m.o.'s are localized mainly on the metal. Thus fewer than 0.25 electron pair is accepted per CO, rather than 0.5 electron pair per CO as has been proposed.

It should be possible, in principle, to apply the force constant–bond order relationship (6.8 mdynes/Å. per unit of bond order) to the direct determination of the π-accepting ability of CO, *e.g.*, in $Mo(CO)_6$, from the "approximate harmonic" force constant for $Mo(CO)_6$[8,9] and the force constant for CO gas.[10] These values are, respectively, 18.12 and 19.02 mdynes/Å., corresponding to a decrease of 0.13 unit of bond order from CO to $Mo(CO)_6$. It cannot be inferred, however, that the bond order for CO coordinated such that there is no $d\pi$–$p\pi$ back bonding, *e.g.*, for a hypothetical complex $OC–BF_3$, will be the same as that for free CO. Removal of an electron from CO to give CO^+ results in an increase in the CO stretching force constant (19.8 mdynes/Å. *vs.* 19.0 mdynes/Å.),[10] and thus it is to be expected, upon formation of an OC–M σ bond as in the $OC–BF_3$ example, that the CO stretching frequency and force constant should increase somewhat from their values for gaseous CO. For example, the carbonyl stretching frequency (2152 cm.$^{-1}$)[11] for $[Pt(CO)Cl_2]_2$ (*vs.* 2143 cm.$^{-1}$ in free CO)[12] has been interpreted as arising from approximately cancelling contributions of σ donation and π acceptance by CO to the CO stretching frequency for this complex.[13] The π-accepting ability of CO in $M(CO)_6$ should therefore be somewhat greater than 0.13 electron pair.

The CO stretching frequencies for the isoelectronic hexacarbonyls $Mn(CO)_6^+$, $Cr(CO)_6$, and $V(CO)_6^-$ are 2090, 1986, and 1859 cm.$^{-1}$, respectively,[14] and thus those in $V(CO)_6^-$ accept more charge than do those in $Cr(CO)_6$. This observation is clearly incompatible with the acceptance of 0.5 electron pair by CO in $Cr(CO)_6$, as it would entail the acceptance of more $d\pi$ electrons in $V(CO)_6^-$ than are available. If the limits of $d\pi$–$p\pi$ charge acceptance by CO in $Mn(CO)_6^+$ and $V(CO)_6^-$ are arbitrarily set at the minimum and maximum possible values, *i.e.*, at 0.0 electron pair accepted in $Mn(CO)_6^+$ and at 0.5 electron pair accepted in $V(CO)_6^-$, it should be possible, from the force constants of these ions, to set upper and lower limits within which the charge-accepting ability of CO in a group VI-B metal carbonyl must fall. Unfortunately, the Raman frequencies for $Mn(CO)_6^+$ and $V(CO)_6^-$ are not available, and thus the desired force constants cannot be calculated directly. Values for the requisite force constants can, however, be calculated from the CO stretching frequencies for the T_{1u} infrared-active modes of $Mn(CO)_6^+$ and $V(CO)_6^-$ and the corresponding secular equation, $\lambda = \mu(k_2 - 2k_i)$,[3] if a second relationship between k_2 and k_i can be obtained. Figure 1 shows the relationship obtained when the *trans*-CO stretching force constant (k_2) is plotted against k_i for 34 representative $M(CO)_{6-x}D_x$ derivatives of Mn and Mo.[1,15,16] From this relationship the force constants $k_2 = 18.0$, $k_i = 0.21$ and $k_2 = 14.9$, $k_i = 0.45$ for $Mn(CO)_6^+$ and $V(CO)_6^-$, respectively, may be calculated. Applying the force constant–bond order relationship to these values yields a π-accepting ability for CO in $M(CO)_6$ of $0.22 < M(CO)_6 < 0.26$ electron pair, in substantial agreement with the π-accepting ability estimated above through a comparison of the force constants for $Mo(CO)_6$ and CO. It should be noted that a moderate error in the second relationship between k_2 and k_i will have only a limited effect on the inferred π-accepting ability; an error of 0.05 in k_i approximates 0.015 unit of bond order. Thus from the evidence cited, ~0.2 electron pair appears to be the best estimate of the π-accepting ability of each CO in $M(CO)_6$; the observed decrease in CO bond order of 0.5 from $Mo(CO)_6$ to $Mo(CO)_3(dien)$ upon which the estimate of 0.5 electron pair was based appears to be fortuitous.

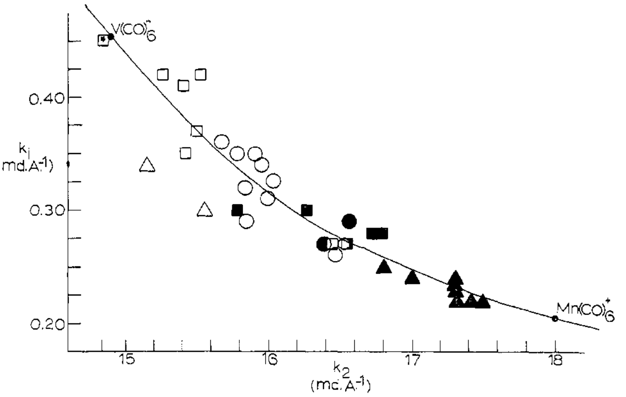

Figure 1.—Relationship between k_2 and k_i for representative $M(CO)_{6-x}D_x$ derivatives of Mo and Mn. Because of the greater availability of CO stretching data, Mo rather than Cr derivatives were chosen. CO stretching frequencies and force constants appear not to vary significantly among Cr, Mo, and W derivatives: ○, $Mo(CO)_6$; O, $Mo(CO)_5D$; △, *trans*-$Mo(CO)_4D_2$; □, *cis*-$Mo(CO)_4D_2$, **cis*-$W(CO)_4D_2$; ●, *trans*-$Mo(CO)_3D_3$; ▲, $Mn(CO)_5D$; ■, *trans*-$Mn(CO)_3D_2Br$.

Barinskii and Nadzhakov in a k-edge absorption study on $Cr(CO)_6$[17] have concluded that the net charge

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[6] H. B. Gray and N. A. Beach, *J. Am. Chem. Soc.*, **85**, 2922 (1963).

[7] The author is indebted to a referee for pointing out that Gray and Beach, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., 1964, have, on the basis of a m.o. treatment, calculated a value of *ca.* 0.1 electron pair accepted per CO in $Cr(CO)_6$; all metal–carbon, metal–oxygen, and ligand–ligand interactions were included in the calculation. In the present paper, the possible effect of $\pi^b{}_{CO} \rightarrow d\pi$ donation has been neglected. This author believes that the agreement between the value of Gray and Beach and the 0.2 proposed here is acceptable, when the limitations of the methods used to obtain them are taken into consideration. The charge on Cr was calculated by Gray and Beach to be +0.35, in good agreement with the value cited by R. L. Barinskii and E. G. Nadzhadov, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **24**, 407 (1960).

[8] L. H. Jones, *J. Chem. Phys.*, **36**, 2375 (1962).

[9] L. H. Jones, personal communication.

[10] L. H. Jones, *J. Mol. Spectry.*, **9**, 130 (1962).

[11] R. S. Nyholm, *Proc. Chem. Soc.*, 273 (1961).

[12] G. Herzberg, "Spectra of Diatomic Molecules," 2nd Ed., D. Van Nostrand and Co., Inc., Princeton, N. J., 1950, p. 62.

[13] E. M. Shustorovich, *Zh. Strukt. Khim.*, **3**, 103 (1962).

[14] W. Beck and R. E. Nitzschmann, *Z. Naturforsch.*, **17b**, 577 (1962).

[15] G. R. Dobson, I. W. Stolz, and R. K. Sheline, *Advan. Inorg. Chem. Radiochem.*, in press.

[16] J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 389 (1965).

[17] R. L. Barinskii and E. G. Nadzhakov, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **24**, 407 (1960).

on Cr is +0.4, and thus the σ-donating and π-accepting abilities of CO in $M(CO)_6$ appear to differ rather little.

The results obtained here yield physically reasonable bond order–bond length relationships[2] in these complexes. The plot of Mo–C bond order against bond length using ~1.2 and ~1.7 as the bond orders in $Mo(CO)_6$ and $Mo(CO)_3$(dien), respectively, is comparable in its essential features to other such curves. A CO bond order of ~2.3 in $Mo(CO)_3$(dien) also is consistent with the CO bond lengths reported (1.153 ± 0.016 Å.).[2] Cox and Jeffrey[18] have compiled a list of eleven C=O bond lengths, which vary from 1.14 to 1.22 Å. The mean was 1.19 Å. Vaughan and Donohue[19] give a value of 1.20 Å. for the length of a pure C=O double bond from the fit obtained with Pauling's bond order–bond length relationship.[20] Thus it is entirely reasonable that a bond length of 1.15 Å. should correspond to a bond order of ~2.3 rather than 2.0, especially since C–O bond lengths should vary little for bond orders between 2 and 3.[2]

Acknowledgments.—The author thanks Mr. Larry W. Houk for valuable assistance, and Drs. L. H. Jones and Heinz Haas for rewarding discussions.

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[18] E. G. Cox and G. A. Jeffrey, *Proc. Roy. Soc.* (London), **A207**, 110 (1951).

[19] P. Vaughan and J. Donohue, *Acta Cryst.*, **5**, 530 (1952).

[20] L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1948, p. 175.

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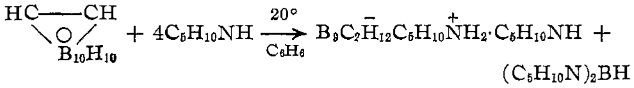
Comments on the Reaction of Amines with 1,2-Dicarbaclovododecaborane(12)

Sir:

Zakharin and Kalnin[1] recently described the facile degradation of 1,2-dicarbaclovododecaborane(12) with piperidine to produce a piperidinium salt of the corresponding dodecahydrodicarbaundecaborate(1−) which contains an additional molecule of piperidine. When



$$\underset{B_{10}H_{10}}{HC—CH} + 4C_5H_{10}NH \xrightarrow[C_6H_6]{20°} B_9C_2\overset{-}{H}_{12}C_5H_{10}\overset{+}{N}H_2\cdot C_5H_{10}NH + (C_5H_{10}N)_2BH$$

heated under vacuum, this product eliminated one mole of piperidine and produced the simple piperidinium salt. The Russian workers consequently suggested that the loosely bound piperidine molecule is attached to the dodecahydrodicarbaundecaborate(1−) anion by a weak dative B–N bond. The resulting complex would be isoelectronic with a hypothetical $B_{11}H_{13}^{-4}$ ion.

In view of our recent investigations of the chemistry of dicarbaundecaborane(13),[2–4] we became intrigued by the possibility that the weakly-bound piperidine molecule was actually present in the crystalline phase as a hydrogen-bonded complex with piperidinium ion and not directly attached to the dodecahydrodicarbaundecaborate(1−) ion. We have examined the ^{11}B n.m.r. spectrum of authentic piperidinium dodecahydrodicarbaundecaborate(1−) in piperidine solution and in 95% ethanol solution. Comparison of the resulting spectra with the ^{11}B n.m.r. spectrum of the trimethylammonium salt of dodecahydrodicarbaundecaborate(1−) in 95% ethanol solution proved the three spectra to be identical in all respects with the characteristic resonances shown in Table I. In view of these results, we conclude that the ubiquitous piperidine molecule is not bonded to the dodecahydrodicarbaundecaborate(1−) anion, but is held in the crystal lattice by hydrogen bonds (or less specific interactions). Only the rarest of coincidences would allow the ^{11}B n.m.r. spectrum of a $B_9C_2H_{12}(amine)^-$ complex to be identical with that of the uncomplexed $B_9C_2H_{12}^-$ ion.

TABLE I

^{11}B N.M.R. CHEMICAL SHIFTS RELATIVE TO TRIMETHYL BORATE

$B_9C_2H_{12}^-C_5H_{10}\overset{+}{N}H_2\cdot C_5H_{10}NH$		$(CH_3)_3\overset{+}{N}HB_9C_2H_{12}^-$
Piperidine	95% ethanol	95% ethanol
26.0	26.5	26.3
32.1	32.4	32.5
37.0	37.5	37.7
42.4	43.4	43.2
50.2	51.2	51.8
55.6	57.3	57.3

We have recently extended the utility of the piperidine degradation of icosahedral carboranes by quantitatively converting 1-phenyl-1,7-dicarbaclovododecaborane(12) to the corresponding dodecahydrodicarbaundecaborate(1−) ion[3] with this reagent in benzene at the reflux temperature.

Acknowledgment.—This work was generously supported by the Army Research Office (Durham).

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[1] L. I. Zakharin and V. N. Kalnin, *Tetrahedron Letters*, **No. 7**, 407 (1965).

[2] R. A. Wiesboeck and M. F. Hawthorne, *J. Am. Chem. Soc.*, **86**, 1642 (1964).

[3] P. M. Garrett, F. N. Tebbe, and M. F. Hawthorne, *ibid.*, **86**, 5016 (1964).

[4] M. F. Hawthorne, D. C. Young, and P. A. Wegner, *ibid.*, **87**, 1818 (1965).

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