show that the phosphorus atoms are virtually coupled, giving rise to 1:2:1 triplets. An X-ray structural determination of *sym*-$[CH_3PC_6H_5Fe(CO)_3]_2$[7] demonstrated that the phenyl groups are parallel to the $C_2$ axis (the phosphorus–phosphorus distance in this complex is 2.864 Å). The proton nmr of this sym isomer exhibits a methyl resonance at $\tau$ 8.08. In $[(CH_3)_2PFe(CO)_3]_2$, two methyl resonances occur at $\tau$ 8.07 and 8.48, respectively. The higher methyl resonance ($\tau$ 8.48) probably corresponds to those methyl groups parallel to the $C_2$ axis (occupying the position of the phenyl group in *sym*-$[CH_3PC_6H_5Fe(CO)_3]_2$) and corresponding to the $F_b$ fluorines in this new complex. This shift to higher magnetic fields was explained on the basis of mutual through-space shielding of the methyl groups. The van der Waals radius of a methyl group (*ca.* 2.0 Å[10]) is sufficiently large to permit an electronic interaction at the distances involved (*ca.* 3.0 Å). In addition, it is noted that in a mixture of isomers of $[CH_3PC_6H_5Fe(CO)_3]_2$, the higher field of the two observed phenyl resonances ($\tau$ 3.10 and 2.57) belongs to the sym isomer described above. It is thus reasonable to assume that the higher of the two PF doublets (+55 ppm) arises from the $F_b$ atoms. The van der Waals radius of fluorine (1.35 Å[10]) is sufficiently large to permit the postulated through-space interaction.

No coupling of the phosphorus atoms in $[F_2PFe(CO)_3]_2$ was observed in contrast to the methylphosphido complexes.

Unlike the organophosphorus and organosulfur complexes cited above which show only three or four bands in the terminal carbonyl region of the infrared, the infrared spectrum of $[PF_2Fe(CO)_3]_2$ in cyclohexane solution shows five carbonyl bands ($\nu_{CO}$ 2104 (m), 2065 (m), 2042 (s), 2031 (s), and 2018 (s) cm$^{-1}$). There are also two PF stretching frequencies at 867 (m) and 853 (m) cm$^{-1}$. This number of bands agrees with the maximum number allowed by simple symmetry arguments, since under $C_{2v}$ symmetry five carbonyl bands are infrared active (*i.e.*, $2\ A_1 + 2\ B_1 + B_2$). The occurrence of these five bands supports the contention that the stretching frequencies of the carbonyl groups are strongly coupled through the metal–metal bond and/or the $PF_2$ groups.

The mass spectrum of $[F_2PFe(CO)_3]_2$ gave a peak corresponding to the parent molecular ion at 418 (based on the most abundant isotope) which agrees with the calculated value. The fragmentation pattern is similar to that of other carbonyl species, namely, loss of six carbon monoxide groups followed by a breakup of the $F_4P_2Fe_2$ framework. The degradation of the $F_4P_2Fe_2$ framework occurs by two pathways. The first is the loss of fluorine, followed by symmetric cleavage of $P_2Fe_2$ moiety. The second path is the symmetric cleavage of $F_2P_2F_4$, followed by the loss of fluorine.

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# [Alkyl(fluorocarbon)phosphine]nickel Carbonyls. Effect of Bond Competition upon Ligand-Exchange Equilibria[1]

By Dae-Ki Kang and Anton B. Burg*

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It has been considered for many years that phosphorus(III) compounds may participate in both $\sigma$-donor and $\pi$-acceptor bonding in transition metal complexes. However, the relative importance of the $\sigma$ and $\pi$ bonds in any specific case has been controversial and difficult to judge.[2] For improved understanding of such bonding situations, there is a need for many further examples of ligand-displacement equilibria, so chosen as to contribute efficiently to the development of general principles.

The equilibria here studied were of the types

$$2LNi(CO)_3 \rightleftarrows L_2Ni(CO)_2 + Ni(CO)_4 \tag{1}$$

$$[(CF_3)_3P]_2Ni(CO)_2 + L \rightleftarrows L(CF_3)_3PNi(CO)_2 + (CF_3)_3P \tag{2}$$

$$L(CF_3)_3PNi(CO)_2 + L \rightleftarrows L_2Ni(CO)_2 + (CF_3)_3P \tag{3}$$

wherein for (1) the ligand L was $(CF_3)_3P$, $CH_3P(CF_3)_2$, or $C_2H_5P(CF_3)_2$, and for (2) and (3) L was $CH_3P(CF_3)_2$, $C_2H_5P(CF_3)_2$, $i$-$C_4H_9P(CF_3)_2$, or $(C_2H_5)_2PCF_3$. The steric effects of these ligands were such as to minimize displacement of CO from the dicarbonyls, but the constants for (2) and (3) seemed not to be sterically affected except when L was $i$-$C_4H_9P(CF_3)_2$.

From the general lore of phosphine bases, it was expected that substitution of an alkyl group for $CF_3$ on P would increase the $\sigma$-bond energy by more than the decrease of $\pi$-bond energy, but there was a possibility that one of the mixed phosphines would show a maximum overall bonding power. Actually, $K_2$ and $K_3$ increased regularly with replacement of $CF_3$ by ethyl groups.

More interesting is the idea that equilibria of the type

$$L_2M(CO)_n + L'_2M(CO)_n \rightleftarrows 2LL'M(CO)_n \tag{4}$$

normally will favor the product, because the competition among different ligands for $\sigma$- and $\pi$-bonding opportunities will not decrease the total bond energy as seriously as such competition between the same ligands will do. This idea, which may be regarded as a generalization of the "ROQ rule,"[3] contributes to the argument against any exact arrangement of ligands in their order of $\sigma$- or $\pi$-bonding power, even for the same central atom. The present results are confirmatory, for we can write $K_4 = K_2/K_3$ and so obtain $K_4$ values of 30, 20, and 20 for three different L's, with $L' = (CF_3)_3P$.

Such bond competition may concern the ligand→metal dative $\sigma$ bonds to the extent that more variety of hybridization in these bonds may be advantageous, but competition for the use of the metal d electrons

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[10] F. A. Cotton and G. Wilkinson, "Advances in Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966.

[1] We are grateful to the National Science Foundation for support of this research through Grant No. GP-17472.

[2] C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2953 (1970), and numerous earlier references there cited.

[3] A. B. Burg, *Accounts Chem. Res.*, **2**, 357 (1969).

seems more important. The ligand CO can employ these in two ways: for $\sigma$-acceptor action by the C–O $\sigma$-antibond orbital or for $\pi$-acceptor action by the C–O $\pi$-antibond orbitals. For all of these, antibond orbitals are important on the metal side of the carbon. A phosphine ligand, however, can have only $\pi$-acceptor action for the metal d electrons, by means of the P 3d and P–R $\sigma$-antibond orbitals, contributing to the same valence cone; both increase in importance with more electronegative R groups. The effect is that the $K_1$ values strongly favor $LNi(CO)_3$: it appears that the competition of L + 3CO in one molecule works less against the total bond energy than 4CO and 2L + 2CO in its disproportionation products.

## Experimental Methods and Results

**Synthesis of Phosphines.**—The ligands $RP(CF_3)_2$ were made from $(CF_3)_2PCl$. The calculated proportion of $Zn(CH_3)_2$, acting during 12 hr at −20° (sealed tube), led to a 90% yield of pure $CH_3P(CF_3)_2$. A slight excess of $Pb(C_2H_5)_4$ (sealed tube, 110°, 24 hr) led to a 95% yield of pure $C_2H_5P(CF_3)_2$. A large excess of $Al(i\text{-}C_4H_9)_3$ (sealed tube, 84°, 24 hr) gave only a 16% yield of $i\text{-}C_4H_9P(CF_3)_2$. For $(C_2H_5)_2PCF_3$, a large excess of $Pb(C_2H_5)_4$ was allowed to react with $CF_3PCl_2$, during 2 days at 100° yielding mainly $C_2H_5PClCF_3$; this was fully identified and then treated further with $Pb(C_2H_5)_4$ during 2 days at 160°. The yield of the desired $(C_2H_5)_2PCF_3$ was 21%. Each of these phosphines was purified by high-vacuum distillation methods, with the use of water (and drying by $P_4O_{10}$) where necessary to destroy residual reactants. Each was identified by its known infrared and nmr spectra and sometimes also by vapor-phase molecular weights and mass spectrography.

**Synthesis of Phosphinenickel Carbonyls.**—The compounds $LNi(CO)_3$ were made by the action of the ligand L upon $Ni(CO)_4$ (slightly in excess) at 25° (5–10 hr) in a stopcocked tube into which the reactants had been condensed from the high-vacuum line. For completion of the process, the evolved CO was pumped off (from the reaction tube at −196°) at appropriate intervals. The unused $Ni(CO)_4$ was removed through a −40° U trap under high vacuum. The slight instability of the $LNi(CO)_3$ compounds in the sense of process 1 made it difficult to eliminate the $L_2Ni(CO)_2$ product, but this could be measured by nmr and infrared spectroscopy, and due account of it was taken when the equilibria were measured. The nearly pure samples of $LNi(CO)_3$ could be distilled into the nmr tubes under high vacuum without appreciable decomposition.

The compound $[(CF_3)_3P]_2Ni(CO)_2$ was made according to the literature.[4,5] Its decomposition to colored products was too slow to cause any difficulty. Other compounds required for the reverse approaches to equilibria 1–3 were obtained from the forward processes 2 and 3.

**Infrared Spectra of the Carbonyls.**—The C–O stretching frequencies of the phosphinenickel carbonyls were determined in the vapor phase by means of the Beckman IR7 instrument, with calibrations to 1 cm$^{-1}$. The following results show the expected trends of increasing $\pi$-acceptor strength for phosphines with more electronegative groups:[6] $(CF_3)_3PNi(CO)_3$, 2116, 2062; $CH_3P(CF_3)_2Ni(CO)_3$, 2105, 2046; $C_2H_5P(CF_3)_2$, 2103, 2058; $(CH_3)_2PCF_3Ni(CO)_3$, 2081, 2004;[2] $(CH_3)_3PNi(CO)_3$ solution in $H_2CCl_2$, 2064, 1982;[2] $[(CF_3)_3P]_2Ni(CO)_2$, 2100, 2065; $[CH_3P(CF_3)_2]_2Ni(CO)_2$, 2076, 2034; $[C_2H_5P(CF_3)_2]_2Ni(CO)_2$, 2074, 2031 cm$^{-1}$. The peaks were all reasonably sharp (except for the effects of impurities) but not so well separated as to permit their use for quantitative studies of equilibria.

**Nmr Spectra.**—The $^{19}F$ nmr spectra of compounds related to the equilibrium studies were recorded by means of the Varian HA-100 instrument, operating at 94.1 Mc. The chemical shift values ($\delta$ in ppm) in Table I were measured upfield of $Cl_3CF$ by the tube-exchange method, without correction for diamagnetism, which in the case of the complexes could have been affected by the equilibrium environment. Side bands were used to measure $J$.

TABLE I

$^{19}F$ NMR PARAMETERS RELEVANT TO PROCESS 1

| R | Parameter | L = $RP(CF_3)_2$ | $LNi(CO)_3$ | $L_2Ni(CO)_2$ |
|---|---|---|---|---|
| $CH_3$ | $\delta$ | 55.5 | 64.1 | 64.0 |
| | $J_{FCP}$ | 75.9 | 80.8 | 82.4 |
| $C_2H_5$ | $\delta$ | 56.7 | 61.9 | 61.6 |
| | $J_{FCP}$ | 71.1 | 73.6 | 74.5 |
| $CF_3$ | $\delta$ | 50.8 | 57.4 | 56.6 |
| | $J_{FCP}$ | 85.5 | 89.0 | 90.6 |

The data of Table II concern the components of equilibria 2 and 3 in their equilibrium environments; the $\delta$ values were measured from $(CF_3)_3P$ as an internal standard, requiring addition of 50.8 to convert to the standard $Cl_3CF$. The $C_1$ and $C_2$ columns represent assignments based upon the 3:2 intensity ratio of the bound $(CF_3)_3P$ and $RP(CF_3)_2$ ligands. For the A, B, and C complexes, the half-height widths were greater than for the free ligands or for the $LNi(CO)_3$-type complexes, presumably because of unresolved FCPNiPCF couplings. This effect made it difficult to select peaks completely free from superposition, for accurate determination of $K$ values. For $K_1$ or $K_3$, the reproducibility is ±10%; for $K_2$, ±15%.

TABLE II[a]

$^{19}F$ NMR PARAMETERS FOR EQUILIBRIA 2 AND 3

| | | L | A | B | $C_1$ | $C_2$ |
|---|---|---|---|---|---|---|
| $CH_3P(CF_3)_2$ | $\delta$ | 7.4 | 5.7 | 12.7 | 6.5 | 12.3 |
| | $J_{FCP}$ | 76.6 | 92.2 | 82.0 | 89.3 | 80.0 |
| $C_2H_5P(CF_3)_2$ | $\delta$ | 4.9 | 5.7 | 10.0 | 6.4 | 9.5 |
| | $J_{FCP}$ | 70.0 | 90.7 | 75.7 | 85.8 | 75.1 |
| $i\text{-}C_4H_9P(CF_3)_2$ | $\delta$ | 4.4 | 5.7 | 9.8 | 6.2 | 9.6 |
| | $J_{FCP}$ | 73.3 | 91.9 | 75.9 | 85.8 | 75.4 |
| $(C_2H_5)_2PCF_3$ | $\delta$ | 8.7 | ... | 13.0 | 7.2 | 12.6 |
| | $J_{FCP}$ | 61.6 | ... | 59.8 | 91.4 | 64.0 |

[a] Heading symbols: L = ligand of the type $RP(CF_3)_2$; A = $[(CF_3)_3P]_2Ni(CO)_2$; B = $L_2Ni(CO)_2$; $C_1$ = $(CF_3)_3P$ and $C_2$ = $RP(CF_3)_2$, in $(CF_3)_3PRP(CF_3)_2Ni(CO)_2$.

**Equilibrium Measurements.**—For process 1 the equilibria were approached from both directions: purified samples of $LNi(CO)_3$ or equimolar mixtures of $L_2Ni(CO)_2$ and $Ni(CO)_4$ were condensed into nmr tubes of 2-mm internal diameter (minimizing loss of CO) at −196° and their nmr spectra were observed very soon after melting. Then the drift toward equilibrium was observed by frequent recording of the $^{19}F$ nmr spectra between periods of standing at 25°, until constancy was achieved. For processes 2 and 3, equimolar or 2:1 ratios of the ligands $RP(CF_3)_2$ or $(C_2H_5)_2PCF_3$ were mixed with $[(CF_3)_3P]_2Ni(CO)_2$ and again the establishment of equilibrium was demonstrated by arrival at constant relative intensities of the pertinent $^{19}F$ nmr peaks. Although the reverse processes were not studied, the observations of the rates of approach to equilibrium left no doubt that equilibration was achieved. When the ligands were $CH_3P(CF_3)_2$ or $C_2H_5P(CF_3)_2$, there were traces of unidentified fluorine compounds (possibly $L_3NiCO$) which introduced no appreciable errors. Even after 5 months at 25°, these samples remained colorless and showed no precipitates.

For the determination of the equilibrium constants $K_2$ and $K_3$, the relative intensity of each peak was measured by means of a planimeter, after instrumental integration had proved unsuitable because of overlapping edge areas. It was feasible to measure the area of the nonoverlapping half of an intrinsically symmetrical peak, to one side of a vertical bisecting line. Each of the constants presented in Table III represented an average of at least two sets of measurements. The minimal equilibration times for process 1 were 1–2 hr; for (2) and (3), they were 7, 3, 3, and 10 hr, respectively. Recheck measurements even 1–3 months later showed no changes.

## Discussion

The equilibrium constants at one temperature led to Gibbs free-energy values, but not to exact comparisons of enthalpy values, which would measure the changes of total bond energy. However, our attempts to determine $K$ values at 0 and 41° showed that the $T\Delta S$ values were comparable to the experimental errors

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(4) H. J. Emeléus and J. D. Smith, *J. Chem. Soc.*, 527 (1958).

(5) A. B. Burg and W. Mahler, *J. Amer. Chem. Soc.*, **80**, 2334 (1958).

(6) M. Bigorgne, *J. Inorg. Nucl. Chem.*, **26**, 107 (1964); *Bull. Soc. Chim. Fr.*, 1986 (1960).

TABLE III
EQUILIBRIUM CONSTANTS AT 25° [a]

| | L | | | | |
|---|---|---|---|---|---|
| | $(CF_3)_3P$ | $CH_3P(CF_3)_2$ | $C_2H_5P(CF_3)_2$ | $i$-$C_4H_9P(CF_3)_2$ | $(C_2H_5)_2PCF_3$ |
| $K_1 \rightarrow$ | 47 | 47 | 70 | ... | ... |
| $K_1 \leftarrow$ | 52 | ... | 68 | ... | ... |
| $\Delta G_1$, kcal | −2.31 | −2.28 | −2.51 | ... | ... |
| $K_2 \rightarrow$ | (1) | 69 | 94 | 10 | (High) |
| $\Delta G_2$, kcal | ... | −2.51 | −2.69 | −1.36 | ... |
| $K_3 \rightarrow$ | (1) | 2.3 | 4.7 | 0.5 | 13 |
| $\Delta G_3$, kcal | ... | −0.49 | −0.92 | +0.41 | −1.52 |
| $K_4 = K_2/K_3$ | ... | 30 | 20 | 20 | ... |
| $\Delta G_4$ | ... | −2.02 | −1.78 | −1.78 | ... |

[a] The subscripts for $K$ and $\Delta G$ refer to equilibria 1–4. The arrows refer to forward and backward approaches to equilibrium.

(average, about ±0.3 kcal), meaning that $\Delta S$ never had more than a fairly small effect on the expression $\Delta G = \Delta H - T\Delta S$. This is a reasonable result, for eq 1–4 show no change in the number of molecules, and the reactants and products have the same numbers of bonds between the same elements, so that any change of molecular entropy would be small. Also the entropy of disproportionation, based upon the statistics of "scrambling," would be considerably smaller than would be required to change the trend of $\Delta H$ relative to $\Delta G$. Hence it is reasonable to regard $\Delta G$ as an adequate basis for qualitative comparison of bond energies and for arguments about bond competition.

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# Long-Range Magnetic Interactions in Europium Hexaborides

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Oesterreicher, Mammano, and Sienko[2] have found that $Eu(NH_3)_6$ is ferromagnetic with a Curie temperature of 5.5°K. Surprisingly, successive replacement of europium by diamagnetic ytterbium produces no change in the strength or sign of the ferromagnetic coupling, as would be expected for indirect exchange through conduction electrons. To explain the results, it has been postulated that the conduction band becomes depopulated at low temperatures due to localization of the conduction electrons in 4f or 5d orbitals. An observed increase in effective magnetic moment from 7.90 to 10.16 BM below 50°K supports this hypothesis. Because $EuB_6$ is also ferromagnetic with an almost identical Curie temperature (*i.e.*, 8°K), a magnetic study was undertaken in order to see if the ferromagnetic coupling in $EuB_6$ is also independent of dilution. The fact that $EuB_6$ has a fundamentally different band structure suggested that behavior might be quite different.

The crystal structure[3] of $MB_6$ corresponds to a primitive cubic lattice with an octahedron of boron atoms at each of the cube corners and a metal atom M at the center of the cube. The $B_6$ octahedra are connected to each other by covalent bonds between the neighboring boron atoms on a cube edge, so the result is a rigid-framework structure in which M atoms occupy the holes. Longuet-Higgins and Roberts[4] and, subsequently, Yamazaki[5] examined the energy-band structure and found that the boron lattice can accommodate twenty bonding electrons per $B_6$ octahedron with a finite energy gap between the highest bonding (valence band) and lowest antibonding orbitals (conduction band) of the crystal. In such case, when M is a divalent metal, $MB_6$ at zero temperature would be an insulator, since three valence electrons from each of six boron atoms plus two valence electrons from one metal atom would give just the twenty electrons needed to fill the valence set. When M is trivalent, however, the extra electron from M can only be accommodated in the conduction band; hence, $M^{III}B_6$ would be a metal. Flodmark,[6] from a more detailed calculation which took in more orbitals and interactions with more neighbors, agreed that $M^{III}B_6$ should be metallic but found that $M^{II}B_6$ might also be metallic, since there appears to be incomplete filling of conduction bands for some directions of electron transport. At present, experimental data on single-crystal conductivities are too few to justify a clear choice between the various models. The best single-crystal work, that of Johnson and Daane,[7] indicates that the alkaline earth hexaborides are semiconducting at high temperatures but may be metallic at low.

All the models are in agreement that the valence electrons of the metal atom are transferred to the boron framework. The structure can thus be considered as a simple cubic array of positive ions in a negatively charged boron network. Since, for stability, the identity of the ions appears unimportant, isomorphous dilution of magnetic rare earth ions by diamagnetic ones appears possible. In this investigation, the magnetic behavior of europium ions on dilution with diamagnetic lanthanum ions was examined.

## Experimental Section

**Materials.**—$EuB_6$, $LaB_6$, $La_{0.50}Eu_{0.50}B_6$, and $La_{0.80}Eu_{0.20}B_6$ were prepared by heating appropriate rare earth oxide mixtures with boron at 1700°. Starting materials were 99.9% $Eu_2O_3$ (from Alfa Inorganics), 99.9% $La_2O_3$ (from Michigan Chemical Corp.), and 99.4% 60-mesh, crystalline boron (from Alfa Inorganics). The boron was heated to 100° and the rare earth oxides were heated to 1000° to remove water prior to weighing. Amounts of rare earth oxide and boron appropriate to the reaction $M_2O_3 + 15B \rightarrow 2MB_6 + {}^3/_2B_2O_2$ (where $B_2O_2$ subsequently goes to $B_2O_3$) were loaded under nitrogen into a $ZrB_2$ crucible, which was then enclosed in tantalum and placed in a covered recrystallized-alumina crucible on a nest of $Al_2O_3$ bubble insulation. Sighting holes in the alumina and tantalum covers permitted monitoring, with a calibrated pyrometer, the sample temperature to within ±20°. The reaction mixture was heated in argon for 45 min at 1700°, using an induction furnace. Outgassing was accomplished at 500°, after which the temperature was slowly raised to 1700°. Reaction began at 1500°, as could be noted by evolution of $B_2O_3$.

After a quench through furnace shutdown, the product was reground under nitrogen and reheated at 1700° for another 45 min. It was finally ground, washed with 1 $N$ HCl and with water, passed through a 200-mesh sieve, and dried. X-Ray

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(2) H. Oesterreicher, N. Mammano, and M. J. Sienko, *J. Solid State Chem.*, **1**, 10 (1969).

(3) G. Allard, *Bull. Soc. Chim. Fr.*, **51**, 1213 (1932); L. Pauling and S. Weinbaum, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **87**, 181 (1934); R. Kiessling, *Acta Chem. Scand.*, **4**, 209 (1950).

(4) H. C. Longuet-Higgins and M. de V. Roberts, *Proc. Roy. Soc., Ser. A*, **224**, 336 (1954).

(5) M. Yamazaki, *J. Phys. Soc. Jap.*, **12**, 1 (1957).

(6) S. Flodmark, *Ark. Fys.*, **14**, 513 (1959).

(7) R. W. Johnson and A. H. Daane, *J. Chem. Phys.*, **38**, 425 (1963).