$Cl_2]Cl$ and *trans*-$[Co(i\text{-bn})(en)Cl_2]Cl$ in 85% ethanol–15% water are 0.79 ± 0.04 and 0.58 ± 0.02. In view of our findings, we would like to join Kane-Maguire and MacDermott[7] in emphasizing the importance of chromatographic monitoring in studying reactions of mixed diamine ligand systems.

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Contribution from the Department of Chemistry,
Hunter College of the City University of New York,
New York, New York 10021

Amine–Substituted Iron Tetracarbonyl[1]

By Bernard J. Bulkin and June A. Lynch

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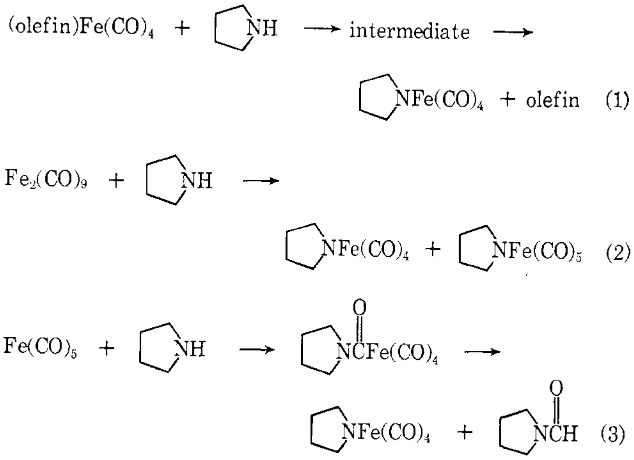
Because nitrogen ligands do not have available low-lying d orbitals, it has been questionable whether or not amines would form complexes with group VIII metals in low oxidation states, analogous to the phosphines, arsines, and stibines, *e.g.*, $(C_6H_5)_3PFe(CO)_4$. Knowledge of the stability and reactivity of the (amine)$Fe(CO)_4$ compounds would shed light on the importance of d-orbital participation in the bonding of the P, As, and Sb analogs.

Edgell and coworkers[2] have reported that when $Fe(CO)_5$ and amines react directly, using the amine itself as solvent, a first species, $>NC(=O)Fe(CO)_4$, is eventually converted into a species having infrared bands at 2045 (w), 1951 (m), and 1924 (s) cm^{-1} in the CO stretching region, proposed to be $>NFe(CO)_4$ (see Figure 4 of ref 2 for spectra). Either the N-formylated amine or the CO gas or both are also formed in the reaction. The final metal carbonyl species was not isolated. We wish to report here the results of certain experiments which confirm that the species yielding the observed spectrum is the proposed amine-substituted iron tetracarbonyl.

It is well known that amines displace olefins as ligands in metal carbonyl compounds. We have therefore synthesized (maleic anhydride)$Fe(CO)_4$ from $Fe_2(CO)_9$ and the olefin according to the method of Weiss and coworkers,[3] as well as (cyclohexene)$Fe(CO)_4$ (which has not been previously described to our knowledge, but can be made by a method identical with that used in ref 3). In each case, when pyrrolidine, C_4H_8NH, is added to a benzene solution of the (olefin)$Fe(CO)_4$, an immediate reaction takes place. This yields an intermediate which, over a period of several hours, is converted into the identical metal carbonyl species reported by Edgell, *et al.*,[2] *i.e.*, bands appear in the infrared spectrum at 2045 (w), 1951 (m), and 1924 (s) cm^{-1} in the CO stretching region. Although we have no evidence as yet, we speculate that the intermediate is either due to an equatorial to axial isomerization of the amine-substituted iron tetracarbonyl or represents a step of higher coordination before free olefin is liberated. In the case of maleic anhydride, if excess amine is present the expected reaction between the anhydride and the amine ensues. No CO is given off in these reactions, nor is there any evidence for any N-formylpyrrolidine being formed.

We have further found that when pyrrolidine is added to $Fe_2(CO)_9$ directly at room temperature, the $Fe_2(CO)_9$ dissolves yielding immediately a species, as shown by infrared spectra, identical with that obtained finally in the olefin-displacement reactions discussed above and in the direct $Fe(CO)_5$–amine reaction after some time. That this species is not due to a reaction of $Fe(CO)_5$ formed in the decomposition of $Fe_2(CO)_9$ is clear for three reasons: (1) the reaction of $Fe(CO)_5$ with pyrrolidine takes 6.75 hr at 60°; (2) direct reaction with $Fe(CO)_5$ yields large amounts of N-formylpyrrolidine, and none is found here; (3) if excess amine is present, we find that it reacts with $Fe(CO)_5$ to give the expected first intermediate, $>NC(=O)Fe(CO)_4$. It is worthwhile to point out that this work again upholds the generalization that $Fe_2(CO)_9$ often reacts as though it were $Fe(CO)_4 + Fe(CO)_5$.

It would appear that the series of reactions



all yielding identical products is excellent evidence for the proposal that this product is indeed amine-substituted iron tetracarbonyl. To date, however, all attempts to isolate the products of reactions 1 and 2 have led to decomposition, probably to polynuclear species. This is in sharp contrast to the phosphine, arsine, and stibine iron tetracarbonyls, which are generally quite stable and unreactive solids.

Experimental Section

$Fe_2(CO)_9$ was prepared by Hg-lamp irradiation of a glacial acetic acid solution of $Fe(CO)_5$ in a Vycor test tube, cooled by

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[2] W. F. Edgell, M. T. Yang, B. J. Bulkin, R. Bayer, and N. Koizumi, *J. Am. Chem. Soc.*, **87**, 3080, (1965).

[3] E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, *Helv. Chim. Acta*, **46**, 288 (1963).

circulating water. All solvents were dried using molecular sieves and were carefully deoxygenated prior to use. Particular care was taken in drying and deoxygenating pyrrolidine, using the method for drying of amines described in ref 2. Maleic anhydride was sublimed *in vacuo* immediately prior to use.

The olefin–iron tetracarbonyls were recrystallized from acetone and then either resuspended in benzene or treated directly with pyrrolidine. The results were the same.

All reactions were carried out with rigorous exclusion of oxygen and moisture. Reaction mixtures were kept in tubes sealed with rubber serum stopples, from which samples could be withdrawn periodically for examination.

Infrared spectra were obtained using the Perkin-Elmer Model 521 dual grating spectrometer, run at *ca.* 1-cm^{-1} spectral slit width in the 2000-cm^{-1} region. Barnes Engineering Co. 0.025 mm KBr demountable liquid cells were used for all spectra.

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
POLYTECHNIC INSTITUTE OF BROOKLYN,
BROOKLYN, NEW YORK 11201

The Polarized Spectrum of Dichlorobis(triphenylphosphine)cobalt(II)

BY C. SIMO[1] AND S. HOLT

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Prominent features of the electronic spectrum of Co^{2+} in tetrahedral coordination have been interpreted, with reasonable success, using crystal field theory.[2-4] Investigations involving the spectroscopic properties of the "tetrahedrally" coordinated Co^{2+} ion have been mainly of two types, however: those which are designed to provide a rigorous test for crystal field theory[2,3] and those which are intended only for identification of a species as "tetrahedral" cobalt.[5,6]

The first type of experiment requires that the species to be investigated be as close to a regular tetrahedron as possible in order to minimize the difficulty involved in sorting out effects due to lowered site symmetry, spin–orbit coupling, and vibrational fine structure.

The second type of experiment requires little more than a knowledge of the molecular formula of the compound to be studied and provides, on most occasions, information as to whether the complex in question possesses a pseudo-tetrahedral structure.

There is, however, lack of detailed experimental information about the electronic structure of tetrahedral Co^{2+} complexes which are fairly strongly distorted from regular. The need for information pertaining to magnitude of splitting of energy levels to be expected upon deforming a regular tetrahedral configuration or by reducing symmetry through introduction of nonequivalent ligands has recently been pointed out in the case of $Co(etu)_2(OAc)_2$.[5]

An early attempt to investigate low-symmetry "tetrahedral" systems was made by Ferguson.[7] Ferguson observed incomplete polarization in the room-temperature crystal spectra of $CoPy_2Br_2$ and $CoPyI_2$ and concluded that the spectra were interpretable only in terms of the next nearest neighbor interaction. In order to help remedy the lack of information in this area, we have undertaken the investigation of the low-temperature polarized spectrum of $((C_6H_5)_3P)_2CoCl_2$.

Crystal Structure

Based on zero- and first-layer Weissenberg photographs, $((C_6H_5)_3P)_2CoCl_2$ and $((C_6H_5)_3P)_2ZnCl_2$ are isomorphous and isostructural with $((C_6H_5)_3P)_2NiCl_2$. $((C_6H_5)_3P)_2NiCl_2$ crystallizes in the space group P2/c with two molecules per unit cell.[8] The site symmetry of the complex is C_2; however, if one ignores the phenyl groups, the effective symmetry is C_{2v}. The C_2 molecular axis is parallel to the *b* crystallographic axis. Both the nickel and the cobalt compounds form a complete range of solid solutions with the isomorphous zinc compound.

Experimental Section

$((C_6H_5)_3P)_2MCl_2$ (M = Zn or Co) were prepared as described by Venanzi.[9] Mixed crystals of $((C_6H_5)_3P)_2(Co,Zn)Cl_2$ were grown by slow evaporation of their nitromethane solution.

Thin crystals of optical quality, for spectra parallel to *a* and *c*, were easily obtained by sectioning along the cleavage plane parallel to the (010) face. Typical crystal dimensions were 3 × 4 × 1 mm. Cobalt concentration was estimated by absorbance of its thiocyanate complex at 625 mμ.[10] The extinction coefficient of the $((C_6H_5)_3P)_2CoCl_2$ in single crystals was estimated according to $\epsilon = al^{-1}d^{-1}c^{-1} \times 10^{-3}$, where *a* is absorbance, *l* is crystal thickness (cm), *d* is crystal density (g/cm^3), and *c* is cobalt concentration (mol/g). Polarized absorption spectra were measured at 298 and 77°K using a Cary Model 14 spectrophotometer. Polarized incident radiation was obtained using a matched pair of Glan–Thomson prisms.

Crystals were mounted on cylindrical brass plugs, which were in turn fixed in a holder and placed in contact with liquid nitrogen. Extinction axes were determined using a polarizing microscope. Correspondence between the extinction and crystallographic axes was obtained by Weissenberg and precession techniques.

Results and Discussion

The 80°K polarized spectrum of $((C_6H_5)_3P)_2CoCl_2$ is shown in Figure 1. Figure 2 contains the spectra of the pure compound taken both in nitromethane solution and in a Nujol mull.

Approximate oscillator strengths of the prominent bands are collected in Table I. These were estimated using the relationship $f = 4.6 \times 10^{-9}\epsilon\Delta\nu$, where ϵ is ϵ_{max} and $\Delta\nu$ is the band width at $\epsilon = {}^1/_2\epsilon_{max}$.[11] As expected for symmetry-allowed transitions, the

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(1) NSF-SDP Postdoctoral Fellow.

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(11) See, for example, T. M. Dunn in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, p 277.