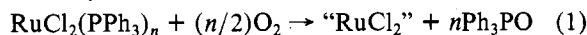
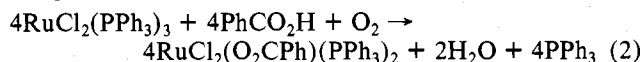


$\text{RuX}_2(\text{PPh}_3)_n$ ($n = 3$ or 4) in particular are highly air-sensitive and undergo rapid oxidation to form dark green or brown products containing triphenylphosphine oxide and/or ruthenium(III) species.^{2,6,9} Previous workers^{6,9} have established that uptake of dioxygen by the $\text{RuCl}_2(\text{PPh}_3)_n$ complexes in benzene solution at ambient temperature corresponds to the stoichiometry



and is accompanied by a color change from orange to green but does not lead to formation of characterizable intermediates or isolable products. In particular, this system affords no positive evidence for the formation of dioxygen adducts.¹⁴ We have found that the stoichiometry of dioxygen uptake by $\text{RuCl}_2(\text{PPh}_3)_3$ at 45 °C is the same as that previously measured at ambient temperature and have observed that subsequent addition of benzoic acid to the oxygenated solution does not afford the complex $\text{RuCl}_2(\text{O}_2\text{CPh})(\text{PPh}_3)_2$. We have also found that uptake of dioxygen during the reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with benzoic acid to form $\text{RuCl}_2(\text{O}_2\text{CPh})(\text{PPh}_3)_2$ amounts to ca. 0.25–0.30 mol O_2 /mol of ruthenium complex. The lower limit is in accord with the reaction



The “extra” oxygen, which is slowly taken up over a period of ca. 90 min, is probably consumed in the oxidation of a small amount of the liberated triphenylphosphine to phosphine oxide. However, ³¹P NMR measurements on the mother liquors after removal of the ruthenium complex establish that whereas substantial quantities of triphenylphosphine are present very little triphenylphosphine oxide is formed. This observation in turn implies that the reaction of carboxylic acids with the ruthenium complexes occurs sufficiently rapidly to prevent significant $\text{RuCl}_2(\text{PPh}_3)_n$ -catalyzed oxidation of triphenylphosphine and that the carboxylato complexes $[\text{RuCl}_2(\text{O}_2\text{CR})(\text{PPh}_3)_2]$ do not act as catalysts for the same reaction. The formation of $\text{RuCl}_2(\text{O}_2\text{CPh})(\text{PPh}_3)_2$ from $\text{RuCl}_2(\text{PPh}_3)_3$ and benzoyl peroxide does not require the presence of dioxygen and probably proceeds by an oxidative-addition mechanism possibly involving the known⁵ binuclear halide-bridged species $[\text{RuX}_2(\text{PPh}_3)_2]_2$.

Acknowledgment. We thank Johnson Matthey and Co. Ltd. for a generous loan of ruthenium trichloride and the S.R.C. for a research studentship award to D.S.M.

Registry No. $\text{RuCl}_2(\text{O}_2\text{CPh})(\text{PPh}_3)_2$, 70046-96-7; $\text{RuCl}_2(\text{O}_2\text{CMe})(\text{PPh}_3)_2$, 70046-97-8; $\text{RuCl}_2(\text{O}_2\text{CC}_2\text{H}_5)(\text{PPh}_3)_2$, 70046-98-9; $\text{RuCl}_2(\text{O}_2\text{CCH}_2\text{Cl})(\text{PPh}_3)_2$, 70084-48-9; $\text{RuCl}_2(\text{O}_2\text{C}-p\text{-C}_6\text{H}_4\text{Cl})(\text{PPh}_3)_2$, 70046-99-0; $\text{RuCl}_2(\text{O}_2\text{C}-o\text{-C}_6\text{H}_4\text{Br})(\text{PPh}_3)_2$, 70047-00-6; $\text{RuCl}_2(\text{O}_2\text{C}-p\text{-C}_6\text{H}_4\text{Br})(\text{PPh}_3)_2$, 70047-01-7; $\text{RuCl}_2(\text{O}_2\text{C}-p\text{-C}_6\text{H}_4\text{OMe})(\text{PPh}_3)_2$, 70047-02-8; $\text{RuCl}_2(\text{O}_2\text{C}-o\text{-C}_6\text{H}_4\text{Me})(\text{PPh}_3)_2$, 70047-03-9; $\text{RuCl}_2(\text{O}_2\text{C}-p\text{-C}_6\text{H}_4\text{Me})(\text{PPh}_3)_2$, 70047-04-0; $\text{RuCl}_2(\text{O}_2\text{C}-p\text{-C}_6\text{H}_4\text{NO}_2)(\text{PPh}_3)_2$, 70047-05-1; $\text{RuBr}_2(\text{O}_2\text{CMe})(\text{PPh}_3)_2$, 70047-06-2; $\text{RuBr}_2(\text{O}_2\text{CPh})(\text{PPh}_3)_2$, 70047-07-3; $\text{RuBr}_2(\text{O}_2\text{C}-p\text{-C}_6\text{H}_4\text{Br})(\text{PPh}_3)_2$, 70047-08-4; $\text{RuBr}_2(\text{O}_2\text{C}-p\text{-C}_6\text{H}_4\text{Me})(\text{PPh}_3)_2$, 70047-09-5; $\text{OsBr}_2(\text{O}_2\text{CPh})(\text{PPh}_3)_2$, 70047-10-8; $\text{OsBr}_2(\text{O}_2\text{C}-p\text{-C}_6\text{H}_4\text{Br})(\text{PPh}_3)_2$, 70047-11-9; $\text{OsBr}_2(\text{O}_2\text{C}-p\text{-C}_6\text{H}_4\text{Me})(\text{PPh}_3)_2$, 70047-12-0; $\text{RuBr}_2(\text{O}_2\text{C}-p\text{-C}_6\text{H}_4\text{NO}_2)(\text{PPh}_3)_2$, 70047-13-1; $\text{RuCl}_2(\text{PPh}_3)_3$, 15529-49-4; $\text{RuBr}_2(\text{PPh}_3)_3$, 15709-75-8; $\text{OsBr}_2(\text{PPh}_3)_3$, 36543-21-2.

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Bis(chlorozinc)tetracarbonyliron: Preparation, Characterization, and Metathetical Reactions with Organotin Chlorides

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Derivatives of $\text{H}_2\text{Fe}(\text{CO})_4$ are commonly made from neutral iron carbonyls¹ or from $\text{Fe}(\text{CO})_4^{2-}$.^{2,3} Vigorous conditions required for reaction of the former with organotin halides frequently give unpredictable products.¹ Little is known about the metathetical reactions of zinc-to-transition-metal bonds or their use in synthetic intermediates. Previous work in our laboratory showed that Zn–Co and Zn–Mn bonds were cleaved efficiently by triorganotin chlorides.⁴ Herein we describe the synthesis of $(\text{ClZn})_2\text{Fe}(\text{CO})_4\text{C}_6\text{H}_{14}\text{O}_3$ and its reactivity with organotin halides.⁵ Chlorozinc and bromozinc derivatives of some molybdenum complexes have been prepared and structurally characterized by Oliver and co-workers.^{6–9}

Experimental Section

All reactions were carried out in modified (two-necked) Schlenk tubes (MST) under an atmosphere of purified argon unless otherwise specified.¹⁰ All melting points were determined in sealed capillary tubes under argon and are corrected. Infrared spectra were obtained with a Perkin-Elmer Model 337 spectrometer. NMR spectra were taken on a Varian A-60A spectrometer calibrated against external Me_4Si . Elemental analyses were performed by the Pascher Microanalytisches Laboratorium, Bonn, West Germany. Analyses of CO were done with the apparatus described by Orchin and Wender.^{11,12} Tin was determined gravimetrically.¹³ *cis*-Bis(chloromercury)-tetracarbonyliron was prepared by the method of Hock and Stuhlman¹⁴ and dried over P_2O_{10} at 56 °C under vacuum. Diglyme was doubly distilled from sodium.

Preparation of Bis(chlorozinc)tetracarbonyliron Bis(2-methoxyethyl) Etherate. $(\text{ClHg})_2\text{Fe}(\text{CO})_4$ (1.28 g, 2.0 mmol), powdered zinc (2.61 g, 40 mg-atoms), and diglyme (40 mL) were stirred together for 18 h during which a yellow precipitate formed. When the mixture was heated to a gentle reflux for 5 min, the precipitate dissolved. After cooling, the mixture was filtered and the solvent was removed by trap-to-trap distillation at 40 °C. The nearly white residue was recrystallized from a mixture of diglyme and toluene yielding 0.56 g (69%) of colorless crystals, mp 162–164 °C dec. Anal. Calcd for $\text{C}_{10}\text{H}_{14}\text{Cl}_2\text{FeO}_3\text{Zn}_2$: C, 23.84; H, 2.80; Cl, 14.08; CO, 22.24. Found: C, 24.29; H, 3.39; Cl, 14.30; CO, 22.5. In one preparation, the zinc

in the zinc amalgam was dissolved in dilute, aqueous HCl and the mercury recovered and weighed (0.388 g, 96.7%).

Preparation of *cis*-Bis(triphenyltin)tetracarbonyliron. Triphenyltin chloride (1.54 g, 4.0 mmol) dissolved in diglyme (15 mL) was added dropwise to a solution of $(\text{ClZn})_2\text{Fe}(\text{CO})_4$ (prepared from 2.0 mmol of $(\text{ClHg})_2\text{Fe}(\text{CO})_4$ but not isolated) in diglyme (40 mL) over a 30-min period. After the addition, the mixture was stirred for 1 h whereupon a small amount of white precipitate was seen. The solvent was removed by trap-to-trap distillation at 40 °C, and the pale yellow solid was redissolved in toluene and filtered to remove insoluble ZnCl_2 . The toluene solution was concentrated to 12 mL and cooled slowly to -62 °C yielding the product (1.11 g, 67%) as light yellow crystals which darkened at 129–132 °C, melted at 148.5–151.5 °C with decomposition then resolidified, and melted with further decomposition at 215–219 °C to give a dark liquid [lit.¹⁵ mp 75 °C, turns brown, 145–150 °C melts with decomposition to a dark liquid]. Anal. Calcd for $\text{C}_{40}\text{H}_{30}\text{FeO}_4\text{Sn}_2$: C, 55.36; H, 3.48; CO, 12.19. Found: C, 55.83; H, 4.04; CO, 13.3.

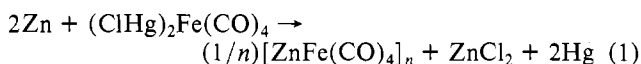
Preparation of *cis*-Bis(μ -*n*-butyltin)tetracarbonyliron. A solution of $(\text{ClZn})_2\text{Fe}(\text{CO})_4$ (prepared from 4.0 mmol of $(\text{ClHg})_2\text{Fe}(\text{CO})_4$ but not isolated) in diglyme (60 mL) was cooled to 0 °C and *n*- Bu_2SnCl_2 (1.22 g, 4.0 mmol) was added with stirring. The mixture was warmed to room temperature, stirred for 30 min, and filtered to remove precipitated ZnCl_2 . The solvent was removed by trap-to-trap distillation at 40 °C, and the residue was extracted twice with hexane to give a yellow solution. The solution was filtered and concentrated until tiny crystals appeared, warmed to dissolve the crystals, and then slowly cooled to -78 °C yielding small, pale yellow crystals (1.11 g, 69%) which were identified by melting point, undepressed mixture melting point with an authentic sample, and infrared spectrum; mp 111–112.5 °C (lit.¹⁶ mp 110–112 °C). No reaction was observed (IR) during 20 h when equimolar amounts of this product and $(\text{ClZn})_2\text{Fe}(\text{CO})_4$ (1.0 mmol) were mixed in diglyme (15 mL).

Preparation of *cis*-Bis(tri-*n*-butyltin)tetracarbonyliron. A solution of $(\text{ClZn})_2\text{Fe}(\text{CO})_4$ (prepared from 2.0 mmol of $(\text{ClHg})_2\text{Fe}(\text{CO})_4$ in diglyme but not isolated) was evaporated to dryness by trap-to-trap distillation (40 °C), and the residue was redissolved in THF (25 mL) and cooled to -78 °C. A solution of *n*- Bu_3SnCl (1.30 g, 4.0 mmol) in THF (5 mL) was added dropwise over a 20-min period. The solution was stirred for 2.5 h at -78 °C. After the mixture was concentrated to 10 mL, hexane (8 mL) was added by trap-to-trap distillation to precipitate most of the ZnCl_2 which was removed by filtration. The solvent was completely removed from the yellow filtrate by trap-to-trap distillation (0 °C), and the residue was redissolved in hexane and filtered to remove additional insoluble material. After again removing the solvent at 0 °C, the product was obtained as a clear, air-sensitive, yellow oil (0.69 g, 75%). The ¹H NMR spectrum of the neat liquid consisted of two complex multiplets: δ 1.15–1.6 (CH_3) with maxima at δ 1.37 and 1.49; δ 1.6–2.2 (CH_2) with maxima at δ 1.72, 1.81, and 1.93. These multiplets were very similar to those of (*n*- Bu)₃SnCl and comprised 98% of the integrated intensity; peaks corresponding to those of diglyme accounted for the remaining area. The thermal instability of the compound precluded acquisition of reliable elemental analyses.

Reaction of $(\text{ZnCl})_2\text{Fe}(\text{CO})_4$ with $(\text{Ph}_3\text{Sn})_2\text{Fe}(\text{CO})_4$. A solution of $(\text{Ph}_3\text{Sn})_2\text{Fe}(\text{CO})_4$ (0.13 g, 0.15 mmol) in diglyme (3 mL) was mixed with 0.9 mL of ~0.18 N $(\text{ZnCl})_2\text{Fe}(\text{CO})_2$ and stirred for 20 h. The IR spectrum of the solution had $\nu(\text{CO})$ at 2065 (vw), 2049 (w), 2038 (vw), 2016 (w), 1985 (vs), 1946 (w), 1900 (s), 1880 (vs), and 1872 (s, sh) cm^{-1} .

Results and Discussion

Previous work in these laboratories demonstrated the generality of the metal-exchange reaction of metal carbonyl derivatives of mercury with zinc and cadmium.¹⁷ In an attempt to prepare $(\text{ClZn})_2\text{Fe}(\text{CO})_4$ from zinc and $(\text{ClHg})_2\text{Fe}(\text{CO})_4$ by a similar metal-exchange reaction in either THF or diglyme, a highly insoluble, yellow precipitate formed. Qualitative analysis showed that the precipitate contained no mercury. This product (eq 1) might be a polymeric material,



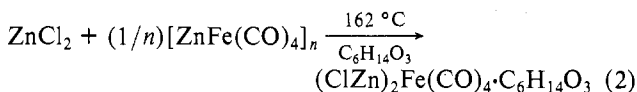
$[\text{ZnFe}(\text{CO})_4]_n$, analogous to $[\text{HgFe}(\text{CO})_4]_n$ and $[\text{CdFe}(\text{CO})_4]_n$.¹⁸ When the mixture was heated, the solid dissolved

Table I. Infrared Spectra of $\text{R}_2\text{Fe}(\text{CO})_4$ Compounds

compd	solvent	$\nu(\text{CO}), \text{cm}^{-1}$
$(\text{ClZn})_2\text{Fe}(\text{CO})_4$	diglyme	2015 m, 1995 m, sh, 1940 s, 1910 s
	THF	2007 m, 1930 s, 1910 s, 1886 s
$(\text{ClZn})_2\text{Fe}(\text{CO})_4 \cdot \text{C}_6\text{H}_{14}\text{O}_3$	Nujol	2025 s, 1964 s, 1933 s, 1909 s, 1872 sh
	$(\text{Ph}_3\text{Sn})_2\text{Fe}(\text{CO})_4$	2065 s, 2003 vs, 1983 vs, 1945 sh
$(\text{Ph}_3\text{Sn})_2\text{Fe}(\text{CO})_4$	diglyme	2067 m-s, 2004 m, 1983 s
	hexane	2067 s, 2013 m, 2008 sh, 1985 s, 1947 vw
	$(n\text{-Bu}_3\text{Sn})_2\text{Fe}(\text{CO})_4$	2051 vs, 1944 s, 1982 s, sh, 1963 vs, 1928 vw
$[n\text{-Bu}_2\text{SnFe}(\text{CO})_4]_2^a$	hexane	2040 vs, 1993 vs, 1980 vs, 1969 w, sh, 1955 w

^a Compare ref 16.

and presumably in the presence of ZnCl_2 formed the solvated species $(\text{ClZn})_2\text{Fe}(\text{CO})_4 \cdot \text{C}_6\text{H}_{14}\text{O}_3$ (eq 2). When the exchange

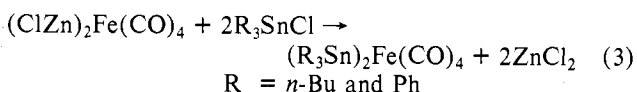


reaction was carried out in THF, the resulting yellow solid was completely insoluble even upon heating of the mixture to reflux. Spectroscopic evidence has been presented for the existence of $\text{ZnFe}(\text{CO})_4$ in aqueous perchlorate solution in equilibrium with several other species.¹⁹ This complex was postulated to form $(\text{ClZn})_2\text{Fe}(\text{CO})_4$ in aqueous chloride solutions¹⁹ (Table I).

The infrared spectrum of $(\text{ClZn})_2\text{Fe}(\text{CO})_4$ has four principal absorptions in the C–O stretching region assigned to the fundamentals of a *cis* octahedral $\text{Fe}(\text{CO})_4$ group in analogy with those of the halomercury derivatives,^{20,21} including $(\text{CO})_4\text{Fe}(\text{HgBr})_2$, the crystal structure of which is known.²²

The use of $(\text{ClZn})_2\text{Fe}(\text{CO})_4$ to synthesize compounds of the type $(\text{R}_3\text{Sn})_2\text{Fe}(\text{CO})_4$ and $[\text{R}_2\text{SnFe}(\text{CO})_4]_2$ has several advantages over the use of $\text{Na}_2\text{Fe}(\text{CO})_4$. The latter compound is pyrophoric,^{3b} while $(\text{ClZn})_2\text{Fe}(\text{CO})_4 \cdot \text{C}_6\text{H}_{14}\text{O}_3$ is stable in air for several hours. In most reactions, however, the chlorozinc complex was not isolated but was used in situ; infrared spectra of solutions of directly prepared $(\text{ClZn})_2\text{Fe}(\text{CO})_4$ indicate that it was produced in nearly quantitative yield.

The new reagent was used to prepare $(\text{Ph}_3\text{Sn})_2\text{Fe}(\text{CO})_4$ and $(n\text{-Bu}_3\text{Sn})_2\text{Fe}(\text{CO})_4$ (eq 3). In the case of $(\text{Ph}_3\text{Sn})_2\text{Fe}(\text{CO})_4$



the yield of isolated material (67%) was more than double that in the literature.¹⁵ In addition, $(\text{ClZn})_2\text{Fe}(\text{CO})_4$ was used to prepare the cyclic compound $[\text{Bu}_2\text{SnFe}(\text{CO})_4]_2$ in high yield.^{1,23}

Bis(tri-*n*-butyltin)tetracarbonyliron, which has been postulated as an intermediate in the synthesis of $[n\text{-Bu}_2\text{SnFe}(\text{CO})_4]_2$ from $\text{Fe}(\text{CO})_5$ and *n*- Bu_3SnCl ,¹⁶ was successfully prepared from **1** and *n*- Bu_3SnCl at low temperatures. This compound was air-sensitive and decomposed fairly rapidly at room temperature under argon.

The infrared spectrum of $(n\text{-Bu}_3\text{Sn})_2\text{Fe}(\text{CO})_4$ is very similar to that of $(\text{Ph}_3\text{Sn})_2\text{Fe}(\text{CO})_4$ (see Table I). The spectra of all of the disubstituted tetracarbonyliron derivatives show four strong bands in the C–O stretching region and are consistent with C_{2v} symmetry and a *cis* configuration about the iron atom.²⁰

The stability of the metathesis products in the presence of $(\text{ClZn})_2\text{Fe}(\text{CO})_4$ was investigated qualitatively by IR spectroscopy; in diglyme $[n\text{-Bu}_2\text{SnFe}(\text{CO})_4]_2$ was unaffected at room temperature whereas $(\text{Ph}_3\text{Sn})_2\text{Fe}(\text{CO})_4$ was nearly completely consumed in 20 h. These observations suggest that

the yield of the latter might be improved by reverse addition.

Acknowledgment. It is a pleasure to acknowledge financial support of this work by the National Science Foundation and the Materials Science Center of Cornell University. We thank the M and T Chemical Co. for samples of organotin compounds.

Registry No. (ClZn)₂Fe(CO)₄, 65991-65-3; (Ph₃Sn)₂Fe(CO)₄, 21868-08-6; [*n*-Bu₃SnFe(CO)₄]₂, 15613-38-4; (*n*-Bu₃Sn)₂Fe(CO)₄, 61788-09-8; (ClHg)₂Fe(CO)₄, 15281-84-2; Ph₃SnCl, 639-58-7; *n*-Bu₂SnCl₂, 683-18-1; *n*-Bu₃SnCl, 1461-22-9.

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π Complexes of Nickel(0) and Ketones. Mechanism of Formation and the Crystal Structure of (Benzophenone)bis(triethylphosphine)nickel

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Transition metals form complexes with a variety of ligands containing a carbonyl functionality. Of these, the β -diketonate complexes, which are among the most common, derive their stability from the formation of chelates with the bidentate ligand. Some simple carbonyl compounds also form stable metal complexes. Thus, monofunctional ketones such as acetone, chloroacetone, and butanone¹ and aldehydes such as acetaldehyde, propionaldehyde, and benzaldehyde,² as well as esters such as methyl formate and ethyl acetate,³ all form stable complexes, especially with divalent transition-metal ions. The carbonyl group in these complexes is usually coordinated through an oxygen atom by σ bonding, and metal ions surrounded by six oxygen atoms in an octahedral array have been described.⁴

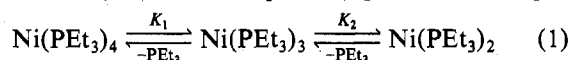
Although rare, there are some examples in which the carbonyl group is π bonded to the metal. Thus, hexafluoroacetone forms a π complex with nickel(0) in which structural data clearly indicate a sidewise coordination of the carbonyl group.⁵ Benzaldehyde and benzophenone also form

stable red complexes with (triphenylphosphine)nickel(0).⁶ More recently, a zerovalent nickel complex of *tert*-butyl isocyanide was reported to afford stable complexes with carbonyl compounds containing electron-withdrawing substituents.⁷ The latter suggests that back-bonding is an important factor in the formation of π complexes of carbonyl compounds with metals, particularly those in low formal oxidation states.

In this study we wish to employ polar substituents on the aromatic ring of benzophenone to probe the mechanism of the formation of π complexes of nickel(0). The parent member of the series has been isolated as a red crystalline compound with composition (Ph₂C=O)Ni(PET₃)₂. The X-ray crystal structure of the π -bonded carbonyl group is compared with the π bonding of other unsaturated ligands.

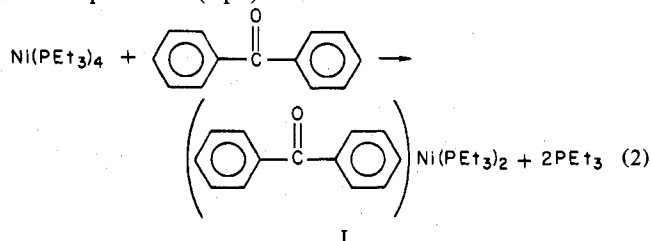
Results and Discussion

The triethylphosphine complex of nickel(0) is isolated as a colorless crystalline solid of composition Ni(PET₃)₄. The complex is labile, and in organic solvents such as tetrahydrofuran (THF), benzene, or hexane it readily dissociates to coordinatively unsaturated species (eq 1). For example,

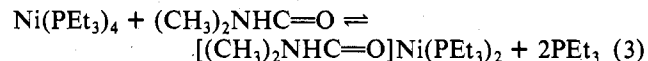


K_1 and K_2 are 1.0×10^{-2} and $<10^{-6}$, respectively, in THF solution. The red color of the solution is associated with Ni(PET₃)₃ absorbing at 500 nm (ϵ 3900).⁸

Product and Stoichiometry. Upon the addition of 1 equiv of benzophenone, the band at 500 nm disappeared with the concomitant growth of a new band at 330 nm. A red crystalline product I (eq 2) could be isolated from this solution.

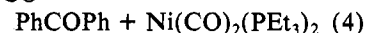


A similar reaction occurred with acetophenone, but we were unable to isolate a crystalline product. The addition of acetone or methyl benzoate to the red solution under the same conditions did not affect either the position, shape, or intensity of the absorption band at 500 nm. The formation constants with these carbonyl compounds are apparently small, since the red color of Ni(PET₃)₃ is not visible in a solution of Ni(PET₃)₄ in the neat solvent (e.g., acetone). Qualitatively, weak π complexes with dimethylformamide (e.g., eq 3) are also in-



dicated by solutions showing a much less intense absorbance at 500 nm compared to that observed in noncoordinating solvents such as THF, benzene, or hexane.

Upon coordination to nickel(0), the infrared stretching frequencies of the carbonyl groups of benzophenone and acetophenone at 1680 and 1690 cm⁻¹, respectively, disappeared.⁹ The complexed benzophenone can be displaced from nickel(0) simply by bubbling carbon monoxide through the solution. The substitution reaction proceeds quantitatively according to eq 4, as indicated by the complete reappearance (PhCOPh)Ni(PET₃)₂ + 2CO \rightarrow



of the carbonyl frequency of free benzophenone as well as the growth of the characteristic bands at 1995 and 1935 cm⁻¹ for Ni(CO)₂(PET₃)₂.¹⁰ The red complex of (benzophenone)bis-(triethylphosphine)nickel is air sensitive and melts between