transition-metal complexes.[23] The use of $Cr(acac)_3$ as a "shiftless relaxation reagent" reduces carbon T_1 times and also helps suppress nuclear Overhauser enhancements.[24] The spectrum was recorded at low temperature to provide "thermal decoupling".[25] (Since ^{55}Mn is 100% natural abundant with I = $^5/_2$, manganese carbonyl resonances are typically very broad at room temperature.) These procedures allowed accurate integrations to be obtained.[26] The intensities of the peaks were measured by planimeter integration, with resonances of the *p*-tolyl and cyclopentadienyl carbons serving as internal standards. The % ^{13}C label per carbonyl site (including natural abundance) was determined to be 8.6% for Mo and 9.5% for Mn. The total % ^{13}C incorporated (above natural abundance) was 7.5% for Mo and 8.4% for Mn.

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Registry No. 1, 83334-34-3; 2, 89828-08-0; 3, 89828-10-4; Mo, 7439-98-7; Mn, 7439-96-5.

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Some Reactions of Tris(2,2,2-trifluoroethyl) Phosphite: A New Ligand for Organometallic Chemistry

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The reactions of $P(OCH_2CF_3)_3$ with three different types of metallocarbonyl compounds $Ni(CO)_4$, $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$, and $(\eta^6\text{-}1,3,5\text{-}(CH_3)_3C_6H_3)Cr(CO)_3$ cleanly form products derived from displacement of CO. The products $(CO)Ni(P(OCH_2CF_3)_3)_3$, $(CO)_2Ni(P(OCH_2CF_3)_3)_2$, $(\eta^5\text{-}C_5H_5)FeI(P(OCH_2CF_3)_3)_2$, and $(\eta^6\text{-}1,3,5\text{-}(CH_3)_3C_6H_3)Cr(CO)_2P(OCH_2CF_3)_3$ are obtained in good yields and are relatively stable. Both thermal and photochemical modes of reaction are observed.

Introduction

When a fluorine atom is substituted in a molecule for another halogen or in particular for a hydrogen atom, significant changes in chemical and physical properties result. With the use of $P(OCH_2CF_3)_3$, we introduce a new ligand into metallochemistry, which allows the incorporation of a large percentage of fluorine into the system so that we can begin to see these changes. We feel that it is important to use these phosphorus(III) compounds, since members of this family have played and still play such an important role in the development of the richness of coordination and organometallic chemistry.[2] Some recent very interesting examples of P(III) usage are to enhance labilization in metal clusters,[3] as substitutional equivalents for carbon monoxide,[4a,b] and for providing the energy for structural reorganization in a cyclopentadienyl metallocarbonyl.[5] These three diverse cases only suggest the scope of possibilities for a new ligand system that contains fluorocarbon moieties in combination with phosphorus(III) which will result in products with significantly different behavior from compounds containing ligands which are derived from hydrocarbon-based starting materials.

While CO is readily substituted by PF_3[6] and fluorophosphine complexes can be converted to fluorophosphite complexes by alcohol solvolysis of metallo derivatives,[7] no direct ligand exchange substitution of CO has been demonstrated by a fluorocarbon derived phosphite prior to our report on the preparation of (η^5-cyclopentadienyl)bis(tris(2,2,2-trifluoroethyl) phosphito)iodoiron(II).[8] The closest example seems to be a displacement by Ruff[9] of $Fe(CO)_5$ from $Fe_2(CO)_9$ forming $(CO)_4FeL$, when L = $F_{3-x}P(OC(CF_3)_2CN)_x$.

We now present evidence for the general use of the title compound as a new, useful ligand in organometallic chemistry.

Results

Reaction of $P(OCH_2CF_3)_3$ with $Ni(CO)_4$. Reaction of 4 equiv of 1 with 2 in pentane gave spontaneous liber-

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[1] The work described herein was accomplished at the University of Idaho where S.M.W. was on sabbatical leave from the University of California, Santa Cruz, CA, 1982–1983 and was presented in part at the 186th National Meeting of the American Chemical Society, August 1983, Washington, D.C.

[2] For some of the scope and variety found from the reactions of P(III) ligands and various organometallic carbonyl compounds see the respective Chapters 10, "Specialist Periodical Reports, Organometallic Chemistry", Royal Society of Chemistry, Publishers, London.

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ation of CO during warmup of the reaction vessel to room temperature. As the reaction proceeded, it was observed

$$4\underset{1}{\mathrm{P(OCH_2CF_3)_3}} + \underset{2}{\mathrm{Ni(CO)_4}} \xrightarrow[40\ ^\circ\mathrm{C}]{\text{pentane}} \underset{3}{\mathrm{(CO)Ni(P(OCH_2CF_3)_3)_3}} + 3\mathrm{CO}\uparrow$$

that slight cooling, not less than 0 °C, produced a phase separation. (Both starting materials are quite soluble in pentane.) It was subsequently observed that the phase separation occurred more easily as the extent of substitution increased. At 40 °C, evolution of CO ceased at a CO/Ni ratio of 2.9:1. This ratio as well as elemental analysis and IR and ^{13}C NMR data from the isolated product proved that 1 equiv of CO remained. The possibility that the large number of fluorine atoms, 27, might have caused sufficient crowding to have extruded the fourth CO was considered, particularly since extraordinarily large ligands such as tricyclohexylphosphine and phenoxyaryl phosphites can stabilize lower coordination numbers for Ni.[10]

$$2\underset{1}{\mathrm{P(OCH_2CF_3)_3}} + \underset{2}{\mathrm{Ni(CO)_4}} \xrightarrow[20\ ^\circ\mathrm{C}]{\text{pentane}} \underset{4}{\mathrm{(CO)_2Ni(P(OCH_2CF_3)_3)_2}} + 2\mathrm{CO}\uparrow$$

It was further observed, during the measurement of CO evolution in the case above, that the first 2 equiv evolved rapidly relative to the third. This was confirmed by an independent experiment that was kept in the dark either at or below 20°. In this case, the reaction stopped at a CO/Ni ratio of 2.1:1 and isolation of the resulting product from the pentane gave a different compound based on its melting point, IR, and NMR data. This compound is a nonvolatile liquid at room temperature, and to date we have been unsuccessful in getting a sample through the microanalytical lab procedure without some decomposition.

Therefore for this Ni(CO)$_4$ system, we see two quite different kinetic levels of substitution with a convenient temperature difference so that the two intermediate compounds in this series can easily be obtained. Light is not required in either case, and even in the presence of light there was no sign of elemental deposition of nickel in the reaction vessel.

Reaction of P(OCH$_2$CF$_3$)$_3$ with (η^5-C$_5$H$_5$)Fe(CO)$_2$I. Reaction of 3 equiv of 1 in methylene chloride with 5 produced CO when irradiated at 20 °C with UV light in a quartz vessel. Thermal reactions were not attempted,

$$3\underset{1}{\mathrm{P(OCH_2CF_3)_3}} + \underset{5}{(\eta^5\text{-}\mathrm{C_5H_5)Fe(CO)_2I}} \xrightarrow[\mathrm{CH_2Cl_2}]{\text{UV}} \underset{6}{(\eta^5\text{-}\mathrm{C_5H_5)FeI(P(OCH_2CF_3)_3)_2}} + 2\mathrm{CO}\uparrow$$

since the reaction proceeded so cleanly with UV illumination. As the reaction proceeded, a color change from dark olive to an intense burgundy red occurred and CO evolution ceased at a CO/Fe ratio of 2.0:1. The ratio as well as elemental analysis, no CO stretching frequency in the IR, and a single ^{31}P NMR signal proved that 2 equiv of CO had been replaced and that the iodine atom was retained. A test on the reaction solution and subsequently on the isolated product with elemental mercury proved negative; therefore the iodine remained bound and nonlabile. The product 6 was quite soluble in CH$_2$Cl$_2$, but after vacuum reduction of the solvent and chilling to −8 °C, deep red crystals slowly formed that were washed with pentane to free them of adhering unreacted 1.

Under these reaction conditions, neither an intermediate level of substitution nor starting material decomposition was observed. The single ^{31}P NMR signal at δ +183.6 removed the question of whether an Arbuzov type rearrangement had occurred. One could have been expected from mediation by the metal–iodine bond such as has been seen to occur so readily by Brill[11a] with (Cp)CoI$_2$CO and P(OCH$_2$CH$_3$)$_3$. Haines[11b] has studied the thermal reaction of 5 with P(OCH$_2$CH$_3$)$_3$ and also finds that the Fe–I bond remains intact but that only monosubstitution is obtained. Brown[11c] has observed the same thermal mode for P(OPh)$_3$ but with UV in refluxing benzene he obtains bissubstitution with 5 and no rearrangement.

Reaction of P(OCH$_2$CF$_3$)$_3$ with (η^6-1,3,5-(CH$_3$)$_3$C$_6$H$_3$)Cr(CO)$_3$. Reaction of 3 equiv of 1 in pentane with 7 gave liberation of CO at 20 °C, when exposed to Pyrex-filtered sunlight or to UV light through quartz.

$$3\underset{1}{\mathrm{P(OCH_2CF_3)_3}} + \underset{7}{(\eta^6\text{-}1,3,5\text{-}\mathrm{(CH_3)_3C_6H_3)Cr(CO)_3}} \xrightarrow[\text{pentane}]{\text{light}} 1\mathrm{CO}\uparrow + \underset{8}{(\eta^6\text{-}1,3,5\text{-}\mathrm{(CH_3)_3C_6H_3)Cr(CO)_2P(OCH_2CF_3)_3}}$$

Evolution continued until the CO/Cr ratio of 2.1:1 was obtained. ^{31}P NMR chemical shifts of 212 and 211 ppm present in the reaction solution indicated the presence of two compounds. Chilling of the reaction mixture at −8 °C slowly yielded a yellow crystalline material that by chemical analysis proved to be the product derived from the loss of one CO, compound 8. The supernatant liquid had a decided green coloration. It is supposed that this other compound with the $\delta(^{31}\mathrm{P})$ + 211 was a bissubstituted product. Since elemental analysis on 8 confirmed the retention of the arene and since the two values for the chemical shifts are so similar, it is further supposed that the arene is retained in the second product as well. This greenish oil has not been purified or further characterized.

Experimental Section

General Data. All reactions were carried out with vacuum line procedures in order to exclude air and moisture as well as to provide a means for measuring the evolved carbon monoxide that was done by repeated cycles of freezing the reaction mixture to −116 °C and expanding the CO into a calibrated vacuum manifold. Conversion of PVT data yielded moles of CO free of background solvent vapor pressure. The solvents methylene chloride, acetonitrile, and pentane had virtually no vapor pressure at −116 °C. They were reagent grade and were used without further treatment. The reactions using Ni(CO)$_4$ were carried out in Pyrex vessels, whereas those using the Fe and Cr reagents 5 and 7, respectively, were contained in quartz with illumination from an Hanovia low-pressure mercury laboratory lamp.

Magnetic resonance spectra were recorded on a JEOL FX-90 Q spectrometer outfitted with a multinuclear probe. Chemical shifts are reported in δ referenced to Me$_4$Si for H and C, 85% H$_3$PO$_4$ for P, and FCCl$_3$ for F. Infrared spectra were recorded through KBr windows on a Perkin-Elmer Model 457 spectrometer, and corrected melting points were obtained from a Thomas-Hoover apparatus. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6 spectrometer with ionization at 17 eV. Elemental analyses on compounds 6 and 8 were obtained from the Microanalytical Lab at the University of Idaho and on com-

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pounds 3 and 8 from the Beller Mikroanalytisches Laboratorium, Gottingen.

The metallic starting materials were from commercial sources and were used directly, except that $Ni(CO_4)$ was trapped at −65 °C immediately before use to free it of CO. The phosphite ligand 1 was prepared according to the literature method.[12] Our values for the boiling point (140 °C (690 torr)) and the ^{31}P NMR (δ(neat) +139) are in accord with data previously reported by Denney.[13]

Preparation of Tris(tris(2,2,2-trifluoroethyl) phosphito)carbonylnickel(0). The phosphite 1 (7.07 g, 21.6 mmol) was added by syringe to 10 mL of pentane in a 200-mL Pyrex vessel fitted with a Kontes O-ring Teflon stopcock. The solution was degassed thoroughly and held under vacuum for the transfer of $Ni(CO)_4$ (0.831 g, 4.87 mmol). During warmup, the tube was shaken vigorously and a homogeneous solution resulted at 0 °C. Carbon monoxide started to evolve overnight while the vessel was below −10 °C. A variety of conditions were utilized, 20 °C in ambient light and 20 °C in filtered sunlight, and CO was continued to evolve until 51% of the available CO had been recovered after 1 day of reaction. Chilling the reaction vessel to 0 °C at this point produced two layers that would reunite at 20 °C with vigorous shaking. Warming the reaction to 40 °C for 27 h yielded an additional 22% of the CO before further evolution stopped. The resulting solution layered at 20 °C but became homogeneous at 40 °C. An additional 10 mL of pentane was added under nitrogen cover, and cooling to 10 °C yielded a white, crystalline solid. Decantation and subsequent washing with pentane followed by vacuum drying produced air-stable, nonhygroscopic crystals of $CONi(P(OCH_2CF_3)_3)_3$. The complex is quite soluble in methylene chloride and has a melting point of 70.5–71.5 °C with no decomposition: IR (methylene chloride) 2982 (w), 2022 (m), 1455 (m), 1418 (m), 1285 (s), 1180 (vs), 1082 (s), 1058 (s), 970 (s), 860 (m), 825 (m), 668 (m), 580 (m), 552 (w), 522 (m), 462 (w) cm^{-1}; NMR spectra were taken in $DCCl_3$; ^{19}F NMR δ −74.2 (t, $^3J_{F-H} = 8.2$ Hz); ^{31}P NMR δ 159.1 (s); ^1H NMR δ 4.2 (q, $^3J_{H-F} = 7.8$ Hz, $^3J_{H-P} = 4.5$ Hz); $^{13}C\{^1H\}$ NMR $OC_c{-}Ni{-}(P{-}(O{-}C_aH_2{-}C_bF_3)_3)_3$, δ_a 61.7 (q, $^2J_{F-C_a} = 38.3$ Hz), δ_b 123 (q, $^1J_{F-C_b} = 277.5$ Hz), δ_c 221 (s). Anal. Calcd for $C_{19}H_{18}F_{27}NiO_{10}P_3$: C, 21.31; H, 1.70. Found: C, 21.57; H, 1.61; an evolved CO/Ni = 2.91:1.

Preparation of Bis(tris(2,2,2-trifluoroethyl) phosphito)dicarbonylnickel(0). The phosphite 1 (1.305 g, 3.98 mmol) was added by syringe to 5 mL of pentane in the same vessel as described above with the same procedures for the degassing and transfer of $Ni(CO)_4$ (0.353 g, 2.07 mmol). During warmup, the tube was wrapped with aluminum foil to exclude all light. After 2 h at 20 °C with shaking, 3.36 mmol of CO had evolved. Four more hours yielded 0.87 mmol and only an additional trace during 12 more hours. The evolved CO/Ni ratio = 2.07:1. Chilling to −100 °C produced a white solid that persisted until above 0 °C before melting to an immiscible oil. The supernatant liquid was removed at −78 °C under nitrogen cover, and the solid was washed with two portions, 1-mL each, of pentane. Last traces of solvent were removed by vacuum pumping, and the solid was warmed slowly and melting was observed at 10–11 °C. No coloration of elemental nickel was seen in the preparation or purification. The supernatant liquid gave a ^{31}P NMR spectrum at δ 163.6 (s). No other resonance was observed. All starting material had been converted. The mass spectrum of the relatively nonvolatile oil yielded *m/e* 328 (parent phosphite) and *m/e* 28 (carbon monoxide). No larger fragments survived the heated inlet system. IR (neat on KBr): 2970 (w), 2900 (w), 2110 (m), 2080 (vs), 2025 (vs), 2000 (vs), 1460 (m), 1421 (s), 1300 (vs), 1175 (vs), 1070 (vs), 970 (s), 860 (s), 825 (m), 666 (s), 582 (s), 560 (s), 522 (m), 460 cm^{-1} (m). Elemental analysis was unsuccessful as some decomposition was observed during the handling procedures.

Preparation of (η^5-Cyclopentadienyl)bis(tris(2,2,2-trifluoroethyl) phosphito)iodoiron(II). The phosphite 1 (0.550 g, 1.67 mmol) was added by syringe to 10 mL of acetonitrile in a quartz 200-mL vessel fitted with an O-ring Teflon stopcock. After η^5-$C_5H_5Fe(CO)_2I$, 5 (0.165 g, 0.54 mmol), was added, the vessel was chilled immediately to −116 °C and thoroughly degassed. No CO evolution was observed from the reaction after the vessel was left sitting at 20 °C overnight in the dark. The vessel was then submerged in a 25 °C water bath and illuminated through the water with a low-pressure Hanovia mercury lamp for 5.5 h, and 1.04 mmol of CO was evolved (96% of theory). (Identical results were obtained from 2.84 mmol of 1 with 1.42 mmol of 5 in methylene chloride.) After vacuum reduction of the solvent and chilling to −8 °C, intensely deep red crystals formed that were washed with pentane to remove any unreacted 1. The complex is quite soluble in methylene chloride, appears to be air and moisture stable, and has a melting point of 68–70 °C with no decomposition. The ^{31}P NMR of the crystalline material, dissolved in CH_2Cl_2, gave only a sharp singlet at δ 183.6. The reaction solution before crystallization also only gave a single resonance at 183.6 ppm, except for the resonance due to the remaining starting material 1. A molecular ion, *m/e* 904, was observed in the mass spectrum, in addition to the following *m/e* values with their relative intensities: 777, M − I, vw; 576, M − $P(OCH_2CF_3)_3$, vs; 447, M − I − $P(OCH_2CF_3)_3$, w; and 248, M − $2P(OCH_2CF_3)_2$, s. Anal. Calcd for $C_{17}H_{17}F_{18}FeIO_6P_2$: C, 22.59; H, 1.88. Found: C, 21.97; H, 1.82.

Preparation of (η^6-1,3,5-Trimethylbenzene)dicarbonyl(tris(2,2,2-trifluoroethyl) phosphito)chromium(0). The phosphite 1 (0.620 g, 1.89 mmol), was added by syringe to 10 mL of pentane in a quartz 200-mL vessel fitted with an O-ring Teflon stopcock. After the (η^6-1,3,5-trimethylbenzene)tricarbonylchromium(0), 7 (0.161 g, 0.63 mmol), was added, the vessel was chilled immediately to −116 °C and thoroughly degassed. After 42 h of UV illumination at 25 °C, CO evolution ceased at 1.35 mmol representing a CO/Cr = 2.1:1. The ^{31}P NMR spectrum on the solution, in addition to showing the excess of 1, showed a major singlet at 211 ppm and a minor singlet at 212 ppm with relative intensity of 4:1. The reaction behaved similarly when the stoichiometry was 7.07 mmol of 1 and 3.54 mmol of 7. After vacuum reduction of the solvent and chilling to −8 °C, yellow crystals were obtained from the mother liquor. The ^{31}P NMR ($CDCl_3$) spectrum of the crystalline material showed a singlet at 212.5 ppm, which corresponds to the resonance of the lesser product. The melting point was ca. 90 °C with decomposition. IR (methylene chloride): 1902 (s), 1845 (s), 1173 (vs), 1060 (s), 970 (s), 856 (s), 582 (w), 520 cm^{-1} (w). Elemental analysis was consistent with the monosubstituted product. Anal. Calcd for $C_{17}H_{18}CrF_9O_5P$: C, 36.70; H, 3.27; F, 30.74. Found: C, 36.85; H, 3.07; F. 31.0. The second compound with the ^{31}P NMR δ value of 211 is presumed to be the bissubstituted product, but it could not be crystallized under these conditions. (Pyrex-filtered sunlight also produced the substitution reaction.)

Reaction of Tris(2,2,2-trifluoroethyl) Phosphite with Dioxygen. Neat phosphite 1 was placed in an NMR tube, and pure dioxygen was bubbled into the liquid through a fine capillary for 30 min at 25 °C. Examination of the ^{31}P NMR spectrum showed only the 139 ppm resonance characteristic of the phosphite starting material. Independent preparation of $(CF_3CH_2O)_3PO$ yielded a ^{31}P NMR δ value of −2.9.

Reaction of Tris(2,2,2-trifluoroethyl) Phosphite with Methyl Iodide. In CH_2Cl_2 solvent in a NMR tube, one drop of 1 and two drops of CH_3I were added. Examination of the ^{31}P NMR spectrum showed only the 139 ppm resonance characteristic of the phosphite starting material. Neither quarternization nor rearrangement was observed.

Discussion

From the study of three different metallocarbonyl systems, we have found that tris(2,2,2-trifluoroethyl) phosphite is an effective substituting ligand for carbon monoxide and it subsequently joins the family of phosphorus(III) compounds that have shown this ability. It has further been seen from these experiments that the behavior exhibited by this fluorocarbon-derived phosphite allows for much greater experimental ease than is the case with its hydrocarbon-derived analogues.[14] This improved behavior is seen in the relatively high degree of thermal, oxygen, and moisture stability of the starting material and

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its products. We attribute these significant and beneficial changes in the characteristics of our system as being due to the presence of the relatively large number of fluorine atoms in the products. One very significant feature is the decrease in hydrocarbon solubility as substitution progresses. Several particular points that arose from the experiments need to be discussed.

Whereas $Ni(P(OCH_2CH_3)_3)_4$ can be directly prepared by displacement of CO from $Ni(CO)_4$[15a] or from the reductive substitution reaction of NiX_2 with $P(OCH_2CH_3)_3$,[15b] the reaction of **2** with **1** stops at 40 °C at trissubstituion, the product of which is further stable to its melting point of 71 °C. It seems from the ease of the loss of the first 2 equiv of CO that the decreased basicity of **1** vs. $P(OC_2H_5)_3$ does not totally account for the lack of complete substitution. Possibly a higher reaction temperature, a more fluorophilic solvent system, or certain steric factors are involved with the reluctance for total substitution. Nevertheless, retention of the carbonyl moiety provides a site for further elaboration.

At present we are beginning to learn about the nature of bonding between the metal and the fluorophosphite. The stability of the products suggests reasonable bond strength. Since oxidative addition[13] can be carried out with **1** to produce a phosphorane, the lone pair of electrons on the phosphorus atom of the phosphite must be reasonably active and available; however the contribution of π bonding with the metal, perhaps enhanced by the electron-withdrawing capability of the OCH_2CF_3 groups, is not clear at this time. However the characteristic infrared absorption frequencies of the ligand and the CO, as illustrated by the trissubstituted nickel complex, shed some light on the character of the bonding as well as serve as a useful indicator for complex formation.

We have measured the IR spectrum of the neat phosphite **1**: IR (neat) 1418 (m), 1290 (s), 1180 (s), 1070 (s), 971 (ms), and 855 cm^{-1} (m). One notices that the P–O stretch of 1031 cm^{-1} in $P(OCH_2CH_3)_3$[16] is shifted to higher energy, 1070 cm^{-1}, in tris(2,2,2-trifluoroethyl) phosphite. This is in accord with the electron-withdrawing effect of the fluorine atoms. This effect is also seen in the enhanced π acidity of the fluoro phosphite illustrated in the higher energy shift for $\nu_{CO} = 2022\ cm^{-1}$ in $(OC)Ni(P(OCH_2CF_3)_3)_3$ vs. 1965 cm^{-1} in $(OC)Ni(P(OCH_2CH_3)_3)_3$[17] due to the decrease in back-bonding from Ni to CO in the fluoro complex.

A most interesting contrast developed from the reaction of **5** with **1**. The reaction is very clean even in the presence of 3 equiv of **1**. Brill[11a] has reported that, with $CpCoI_2CO$ and 3 equiv of $P(OC_2H_5)_3$ in CH_2Cl_2, a double Michaelis–Arbuzov rearrangement occurs in which the metal–iodine bond acts as the electrophilic site for the generation of a phosphonium salt followed by rearrangement to a phosphonate. The similarity of **5** with Brill's starting material, as well as an earlier report by Haines[11b] in which he used **5** and saw only monosubstitution under thermal conditions or salt formation and rearrangement with the Fe–Cl equivalent compound, alerted us to the possibility of an Arbuzov rearrangement; however the ^{31}P NMR shows little if any sign of a P(V) resonance in the reaction solution. We believe that this difference in stability of **6**, even in the presence of excess **1**, indicates in this case significantly greater reluctance of the fluoroalkoxy moiety to undergo the Arbuzov type rearrangement than its hydrocarbon analogue. Fox[18] has noted somewhat similar behavior from the greater thermal stability of fluoroalkyl sulfites vs. hydroalkyl sulfites; however Shreeve[19] has seen examples of rearrangements in other reaction systems. This problem remains an interesting one for further study.

The literature contains many examples and much discussion regarding the similarity of bonding between CO and PF_3,[6] but it is difficult at the beginning of the experimental work on this new system to predict the bonding relationship of CO compared with $P(OCH_2CF_3)_3$. The retention of the mesitylene group in the products of the reaction of **7** with **1** raises an important question regarding the relative ability of σ donors to displace π-bonded vs. σ-bonded moieties.

Two modes of substitution in an arene metallocarbonyl have been observed and discussed. Silverthorne[20a] has reviewed the CO loss with retention of the arene.

$$(arene)Cr(CO)_3 + L \xrightarrow{UV} (arene)Cr(CO)_2L + CO\uparrow$$

L = phosphines, amines, nitriles, sulfides, olefins, etc.

Poilblanc[20b] has further demonstrated and Klabunde[20c] has discussed the utility of using $(arene)M(CO)_3$ and related metallocarbonyl diene complexes as reagents for the retention of the structural geometry of the carbonyl groups during substitution of the arene or diene by a variety of phosphines and phosphites.

$$(arene)M(CO)_3 + 3L \rightarrow \mathit{fac}\text{-}M(CO)_3L_3 + arene$$

$$L = PR_3,\ P(OR)_3;\ R = \text{hydrocarbon moiety}$$

Our finding with the fluorocarbon phosphite is in accord with retention of the arene. We definitely have a second uncharacterized product, but its ^{31}P and ^{1}H NMR chemical shift values suggest that the second product is electronically very similar to the isolated product **8**.

Conclusions

Tris(2,2,2-trifluoroethyl) phosphite has been shown to be a very useful ligand for the displacement of carbon monoxide from a variety of metallocarbonyl compounds. The products are attractive for further chemical studies and illustrate that it will be possible to incorporate large percentages of fluorine into various organometallic systems so that the unique properties that arise due to the presence of fluorine can be observed in this new area of chemistry.

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Registry No. 1, 370-69-4; 2, 13463-39-3; 3, 90029-46-2; 4, 90029-47-3; 5, 12078-28-3; 6, 86940-11-6; 7, 12129-67-8; 8, 90029-48-4.

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