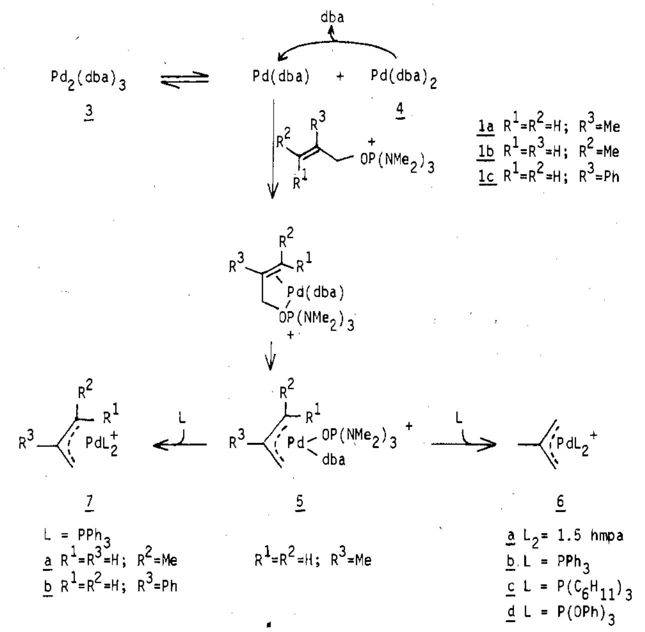
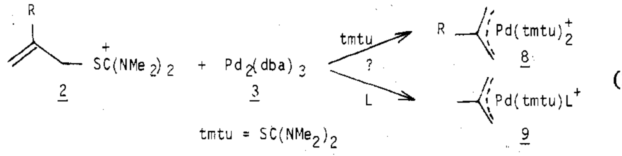
Scheme I



co-workers[10] on the oxidative addition of allyl phenyl ether on nickel(0) compounds, we suggest that the reaction occurs according to Scheme I. Attempts to isolate the intermediate **5** from the reaction mixture have until now failed. Relevant experiments in progress are designed to demonstrate the plausibility of this reaction scheme.

Inspection of Table I shows the expected NMR patterns. However, complex **6d** presents in its ^{1}H NMR spectrum (Figure 1) an upfield shift of the 2-methyl substituent. This shift could be induced by the shielding of the methyl group through either phenyl group(s) of the phosphite ligands or the interaction of the methyl hydrogens with electron-poor palladium cation via an axial coordination as already reported for other palladium complexes[11] or allyliron complexes.[12] Variable-temperature NMR and X-ray crystallographic studies of this compound will be undertaken in order to assign the origin of this shift.

A similar reaction occurs with the (allylthio)uronium salts **2** leading to complexes **8** and, possibly, mixed-ligand complexes **9** although this opportunity has not yet been investigated.



(3)

Finally, it should be pointed out that the preparation of cationic complexes according to the procedure of Powell and Shaw[3a] could be modified and extended to noncomplexing anions other than tetraphenylborate, like ammonium hexafluorophosphate or lithium perchlorate.

Experimental Section

Procedure I: (η^3-2-Methylallyl)bis(triphenylphosphine)palladium(II) Hexafluorophosphate. In a 50-mL Schlenk tube were successively placed Pd$_2$(dba)$_3$ CHCl$_3$[4] (259 mg, 0.25 mM) and ((2-methylallyl)oxy)tris(dimethylamino)phosphonium hexafluorophosphate[6] (190 mg, 0.5 mM). This mixture was degassed by three vacuum-argon atmosphere cycles. Acetonitrile (10 mL) was then added and the reaction mixture stirred under argon. After 45 min, the pale yellow solution was filtered through Celite in order to remove some traces of metallic palladium. Addition of triphenylphosphine (262 mg, 1 mM) followed by concentration of the reaction medium to ca. 2 mL and addition of 50 mL of dry ether led to the precipitation of a white solid. This suspension was stirred for 2 h, and then the solid was filtered off and washed with 3 × 10 mL of ether. The microcrystalline powder was dried under vacuum (yield 383 mg, 92%).

The same procedure was used with dichloromethane in place of acetonitrile.

Procedure II: (η^3-2-Methylallyl)bis(tetramethylthiourea)palladium(II) Hexafluorophosphate. In a 50-mL Schlenk tube were successively placed (η^3-2-methylallyl)chloropalladium(II) dimer (394 mg, 1 mM), tetramethylthiourea (529 mg, 4 mM), and finely powdered ammonium hexafluorophosphate (326 mg, 2 mM). The mixture was degassed by three vacuum-argon atmosphere cycles. Acetonitrile (10 mL) was then added and the reaction mixture stirred under argon. After 15 min, the suspended ammonium chloride was filtered off and the solution concentrated in vacuo to ca. 2 mL. Addition of ether (20 mL) led to the precipitation of the complex which was recovered by filtration and washed with 3 × 10 mL of ether. The microcrystalline powder was dried under vacuum (yield 1.01 g, 89%).

Acknowledgment. We thank the Dêlêgation Generale â la Recherche Scientifique et Technique and the Sociêtê des Produits Chimiques Ugine Kuhlmann for the support of this work.

Registry No. **6a**, 74397-57-2; **6b**, 74397-58-3; **6c**, 74397-60-7; **6d**, 74397-62-9; **7a**, 74411-03-3; **7b**, 74397-64-1; **8a**, 74397-66-3; **8b**, 74397-67-4; **8c**, 74397-69-6; **8d**, 74397-71-0; Pd$_2$(dba)$_3$, 52409-22-0; (η^3-2-methylallyl)chloropalladium(II) dimer, 12081-18-4.

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[11] Postel, M.; Pfeffer, M.; Riess, J. *J. Am. Chem. Soc.* **1977**, *99*, 5623.

[12] Ittel, S. D.; Van-Catledge, F. A.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 6905.

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Iron Carbonyl-Trifluorophosphine Compounds as Photocatalytic Precursors in Isomerization Studies

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Transition-metal carbonyls have long been studied as both stoichiometric and catalytically active species in organometallic reactions; their photochemistry has been actively investigated.[1,2] Soluble transition-metal catalysts offer the advantage of a definite stoichiometry and structure and have been used to elucidate catalytic reactions. The activity of the catalyst can be controlled by variation of the ligands attached to the metal atom, the oxidation state of the metal, or even the metal itself. Understanding the influence of these variables will allow the design of more efficient and more selective catalysts in the future, i.e., catalysts tailored for a given reaction.[3] Inorganic synthetic techniques are now available to afford compounds which will allow such systematic studies.

Several series of metal carbonyl-trifluorophosphine compounds, of the general form M(PF$_3$)$_y$(CO)$_x$, have been prepared and characterized. Phosphorus trifluoride is unique in the world of ligands that replace carbon monoxide in metal carbonyls in that its substitution reactions result in the sequential replacement of carbonyl groups throughout the entire composition range. When there can be more than one isomer for a given composition, all possible isomers will generally exist.

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[1] von Gustorf, E. A.; Leeders, L. H. G.; Fischler, I.; Perutz, R. *Adv. Inorg. Chem. Radiochem.* **1976**, *19*, 65-183.

[2] (a) Strohmeir, W. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 730-737. (b) Wrighton, M. *Chem. Rev.* **1974**, *74*, 401-430.

[3] Henrici-Olivê, G.; Olivê, S. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 105-115.

The compounds are physically and electronically quite similar to the parent carbonyls.[4] Despite similarities among the various carbonyl–trifluorophosphine species, subtle systematic differences do exist.

The reactions of iron carbonyl compounds have been extensively investigated.[5] Schroeder and Wrighton[6a] have shown that iron pentacarbonyl is photocatalytically active in the isomerization of olefins. Thermally catalyzed reactions of $Fe(CO)_5$ are also known.[7]

This note is the first of a series of papers looking into the photocatalytic properties of metal carbonyl–trifluorophosphine compounds. It deals primarily with the isomerization of linear pentenes at ambient temperature with use of the various species in the system $Fe(PF_3)_x(CO)_{5-x}$, where $x = 0$–5.

Experimental Section

The various species of the system $Fe(PF_3)_x(CO)_{5-x}$ were prepared by the thermal and photochemical routes described earlier.[8] They were isolated by gas chromatography, dried by vacuum distillation through P_4O_{10}, sealed under vacuum, and stored at −20 °C until used. 1-Pentene was pure grade from Phillips Petroleum and the *cis*- and *trans*-2-pentene, 98.4 and 99.8%, respectively (GC), were obtained from Chemical Samples Co. The pentenes were purified by stirring with acidified aqueous ferrous ammonium sulfate to remove oxidizing impurities, followed by distillation under nitrogen from calcium hydride. The pentenes were then sealed in evacuated vessels until used.

Samples for irradiation were prepared in a nitrogen atmosphere from a stock solution of the appropriate iron compound and pentene, freeze–pump–thawed 3 times, and sealed. Preparations were designed to exclude moisture and oxygen and minimize exposure to room light. The samples were stored in liquid nitrogen both before being irradiated and while awaiting analysis.

Samples were irradiated continuously in a merry-go-round apparatus using a 450-W medium-pressure Hanovia mercury lamp. The light was filtered with an ammoniacal copper sulfate solution (75.0 g of $CuSO_4 \cdot 5H_2O$ + 100 mL of 58% NH_3/L) which allows transmission in the 400–450-nm region. In addition, a layer of a neutral density filter of 18/20 mesh screen surrounded the jacket. Light intensities were determined by ferrioxalate actinometry[10] to be about 3×10^{-6} einstein min^{-1}. The merry-go-round was modified so that samples could be protected from the light until the lamp warmed up to reach full, stable light intensity. The apparatus was thermostated at 30.0 ± 0.1 °C.

Olefin analysis was done with a Varian-Aereograph Autoprep A-700 gas chromatograph. A 25 ft × 1/4 in. column loaded with 40% β,β'-oxydipropionitrile on 80/100 mesh Chromosorb P was used at ambient temperature.

Results

Table I. Pentene Isomer Composition as a Function of the Concentration of $Fe(PF_3)_2(CO)_3$[a]

concn of iron compound, M	% 1-pentene[b]	concn of iron compound, M	% 1-pentene[b]
9.13×10^{-4}	65.37 ± 0.06	1.83×10^{-2}	31.2 ± 0.2
4.56×10^{-3}	39.8 ± 0.2	9.13×10^{-2}	56.6 ± 0.2
9.13×10^{-3}	26.4 ± 0.2	$4.56 \times 10^{-}$	77.7 ± 0.5

[a] Samples, initially pure, degassed 1-pentene, were irradiated for 3.0 h in parallel in a merry-go-round apparatus at 30 °C by using 400–450-nm radiation at 3×10^{-6} einstein min^{-1}. [b] The isomer ratio of *trans*-2-pentene:*cis*-2-pentene is about 3.5–3.6 for all concentrations.

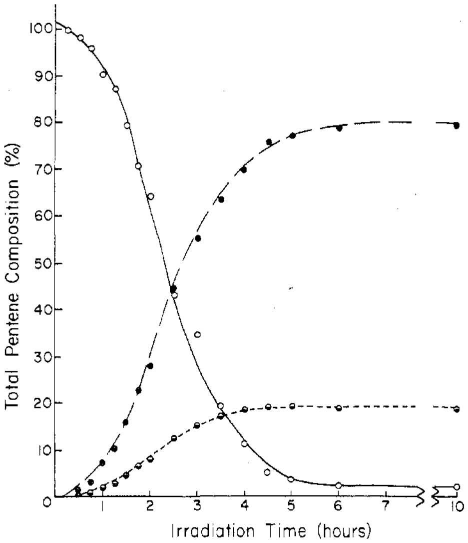

Figure 1. Plot of 1-pentene disappearance (open circles) and *cis*- (half-filled circles) and *trans*-2-pentene (filled circles) formation as a function of irradiation time. Initial conditions: 9.13×10^{-3} M $Fe(CO)_3(PF_3)_2$ in degassed 1-pentene; irradiated at 30 °C in a merry-go-round apparatus by using 400–450-cm radiation.

The olefins 1-pentene and 1-hexene isomerize readily at room temperature when irradiated by light from a medium-pressure mercury lamp in the presence of the carbonyl(trifluorophosphine)iron(0) compounds $Fe(PF_3)_x(CO)_{5-x}$. The reactions yield respectively *cis*- and *trans*-2-pentene or *cis*- and *trans*-2-hexene and -3-hexene. No other major reaction products are ever detected. The pentenes have been studied most extensively owing to the simplicity of product analysis. One stray peak is seen occasionally in the chromatograms. It is, at maximum, 0.2% of the total area, and the substance has not been identified. The isomerization reactions described do not occur upon the irradiation of the olefins in the absence of the iron carbonyl compound, nor do they occur thermally at room temperature in the presence of iron carbonyls.

Variation of the concentration of the initial iron species causes a dramatic effect on the extent of reaction, as shown for $Fe(PF_3)_2(CO)_3$ in Table I. For a fixed period of irradiation, as the initial concentration of the iron compound is increased, the percent of 1-pentene isomerization increases, reaches a maximum and then decreases. None of these solutions initially absorb 100% of the incident radiation. Solutions deepen in color markedly as the isomerization reactions proceed. The iron concentration of 9.13×10^{-3} M (0.1 mol %) was optimal for the diphosphine; that molarity has been pragmatically chosen as the standard concentration for all studies.

A typical plot of pentene concentration vs. time using a constant light intensity is shown in Figure 1 for 9.13×10^{-3} M $Fe(PF_3)_2(CO)_3$ in pure 1-pentene. Three salient features can be noted: first, an induction period, which is followed by a rapid conversion of 1-pentene to *cis*- and *trans*-2-pentene, and a final equilibrium mixture which is the same within

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(6) (a) Schroeder, M. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 551–558. (b) Schroeder, M. A.; Wrighton, M. S. *J. Organomet. Chem.* **1977**, *128*, 345–358.

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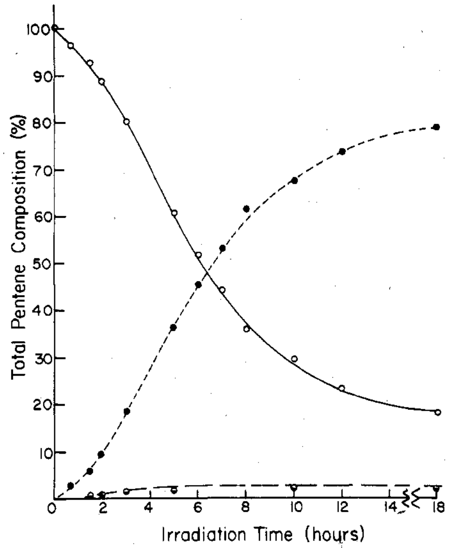

Figure 2. Plot of *cis*-2-pentene disappearance (open circles) and 1-pentene (half-filled circles) and *trans*-2-pentene (filled circles) formation as a function of irradiation time. Initial conditions: 9.46 × 10^{-3} M $Fe(PF_3)_2(CO)_3$ in degassed *cis*-2-pentene; irradiated at 30 °C in a merry-go-round apparatus by using 400–450-nm radiation.

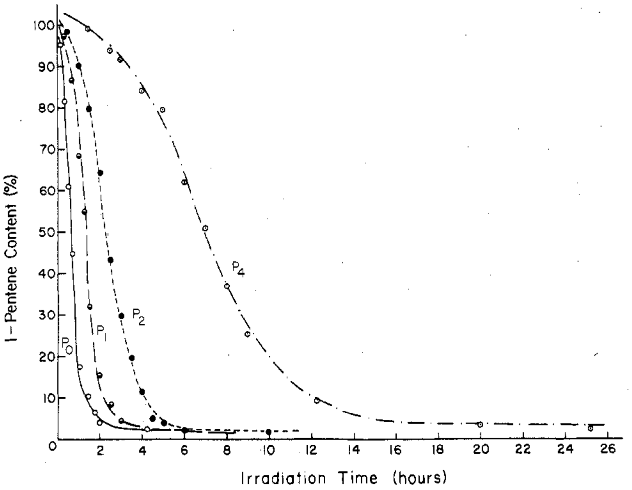

Figure 3. Comparison of the extent of reaction as a function of irradiation time using various iron compounds as catalyst precursors: $Fe(CO)_5$ (open circles); $Fe(CO)_4PF_3$ (half-filled circles); $Fe(CO)_3(PF_3)_2$ (filled circles); $Fe(PF_3)_4CO$ (circles and dots).

experimental error for all iron species. The reaction approaches the thermodynamic equilibrium composition[11] of about 2.3% 1-pentene, 79.0% *trans*-2-pentene, and 18.3% *cis*-2-pentene. Throughout this reaction, the trans/cis ratio is maintained at approximately 4:1. A related reaction profile is seen when starting with either *cis*- or *trans*-2-pentene. A typical example using *cis*-2-pentene and $Fe(PF_3)_2(CO)_3$ is shown in Figure 2. Again the final concentrations represent the thermodynamic equilibrium for a thermal reaction. However, the cis–trans isomerization is slower than the positional isomerization.

A comparison of catalytic properties of the various iron compounds in the system $Fe(PF_3)_x(CO)_{5-x}$, where $x = 0$, 1, 2, and 4, is shown in Figure 3 as a plot of 1-pentene concentration vs. time. Insufficient data were available to construct a complete plot for $Fe(PF_3)_3(CO)_2$. However, the data available clearly indicate that the rate curve falls roughly where expected between the di- and tetraphosphine complexes.

Table II. Examination of the Thermal (Dark) Behavior of the Photogenerated Catalyst

iron compd	irradn time,[a] h	dark time,[b] h	% 1-pentene[c]
$Fe(CO)_5$	0.52	0	61.0
$Fe(CO)_5$	0.52	24	49.1
$Fe(PF_3)(CO)_4$	1.00	0	79.7 ± 0.2
$Fe(PF_3)(CO)_4$	1.00	24	59.9 ± 0.1
$Fe(PF_3)(CO)_4$	1.00	24	64.1 ± 0.2
$Fe(PF_3)(CO)_4$	1.00	24	61.2 ± 0.2
$Fe(PF_3)_2(CO)_3$	1.50	0	84.0 ± 0.2
$Fe(PF_3)_2(CO)_3$	1.50	3.0	69.8 ± 0.2
$Fe(PF_3)_2(CO)_3$	1.50	6.0	71.8 ± 0.4
$Fe(PF_3)_2(CO)_3$	1.50	24	61.2 ± 0.2
$Fe(PF_3)_4CO$	17.5	0	9.3 ± 0.1
$Fe(PF_3)_4CO$	17.5	24	6.1

[a] Samples were irradiated in parallel in a merry-go-round apparatus at 30 °C by using 400–450-nm radiation at 3 × 10^{-6} einstein min^{-1}. All contained 9.13 × 10^{-3} M iron compound in 1-pentene. [b] Stored in the dark at ambient temperature. [c] The remaining percentage is *trans*-2-pentene and *cis*-2-pentene in an approximate 4.1:1 ratio, respectively.

It is the compound $Fe(PF_3)_5$ that presents the surprise. Only 1 or 2% isomerization is found after 42 h of irradiation. Even when both the $CuSO_4$–NH_3 filter solution and the neutral density filter are removed, there is no significant isomerization. We speculate that the isomerization which does occur is due to impurities.[12]

The data in Figure 3 show that there is an induction period for all compounds. We arbitrarily define the induction period as the time required for 5% of the starting pentene isomer to react. The values for the species $Fe(PF_3)_x(CO)_{5-x}$ are 9, 26, 46, 90, and 145 min for $x = 0$–4, respectively. The 90-min value is estimated from limited data.

In spite of the slower rates of reaction and the lengthening induction periods as the PF_3 content of the iron species is increased, the basic nonreactivity of $Fe(PF_3)_5$ is entirely out of line. From a plot of induction period vs. the number of PF_3 groups, one would estimate an induction time for $Fe(PF_3)_5$ of no more than 200–240 min for 5% conversion. Such a conversion is not reached either by 48-h irradiation with the ammoniacal copper(II) sulfate solution as filter or under conditions of far greater intensity such as Pyrex-filtered light irradiation for 40 h. Higher concentrations of $Fe(PF_3)_5$ do not produce a significant increase in isomerization.

The data presented in Table II make it clear that the catalytic species, once it is formed, is capable of catalyzing the reaction in the dark. Although the reproducibility of the dark reaction data is troublesome, there is up to 10–15% transformation of 1-pentene to 2-pentene during the hours that follow irradiation. This represents about 100 turnovers/mol of iron. The dark reaction eventually succumbs to a catalyst poison.

Quantum yields were determined for the various reactions. These calculations assume the initial iron species–pentene solutions absorb 100% of the incident radiation; in each instance they absorb less. Thus, the quantum yields as calculated are *lower limits* and range from 64 for $Fe(CO)_5$ to 6.1 for $Fe(PF_3)_4CO$.

Discussion

Substitution of phosphorus trifluoride into iron pentacarbonyl causes a subtle incremental effect on the photo-

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(11) Bond, G. C.; Hellier, M. *J. Catal.* **1965**, *4*, 1–5.

(12) For purification of $Fe(PF_3)_5$ from $Fe(PF_3)_4(CO)$ by VPC, quite long columns must be used. This results in very long retention times for the compounds with lower degrees of phosphine substitution. If a mixture is used which *presumably* contains only the highest phosphines, then reasonable rates of repetition on the GLC can be used with overlapping cycles. However, this presents the danger of trapping traces of the carbonyl-rich material if they are present.

catalyzed isomerization of linear pentenes. The increasing PF_3 content in $Fe(PF_3)_x(CO)_{5-x}$, where $x = 1$–4, causes these species to become a progressively less effective photochemical catalyst for the isomerization.[13]

Quantum yields which are significantly above unity show the reaction is by Wrighton's definition[14] photocatalytic rather than photoassisted. The thermodynamic equilibrium mixture of isomers is always observed. These data suggest that the catalytic intermediate is generated photochemically and the isomerization reaction is thermal in nature. The sustained isomerization observed during the hours following sample irradiation confirm the thermal nature of the reaction. A comparison of the dark reaction data and the photolysis results for a given iron compound indicates the process is photoaccelerated.

Studies on isomerization of alkenes by photochemical generation of a catalyst from $Fe(CO)_5$ have been investigated by Schroeder and Wrighton.[6a] Reactions, carried out in benzene solution, were characterized by a short induction period and smooth conversion to the equilibrium mixture of isomers. They proposed a mechanism that started with the photochemical reactions

$$Fe(CO)_5 \xrightarrow[\text{alkene}]{h\nu} Fe(CO)_4(\text{alkene}) \xrightarrow{h\nu} [Fe(CO)_3(\text{alkene})]$$

The intermediate $[Fe(CO)_3(\text{alkene})]$, in which alkene could represent 1-pentene, would by the formation of an allyl hydride intermediate, $HFe(\text{allyl})(CO)_3$, yield *cis*- and *trans*-2-pentene. A thermally active intermediate in their scheme[6a] is thought to be $Fe(CO)_3(\text{alkene})_2$. If CO and PF_3 are simply photosubstitutable ligands, then one could replace CO by PF_3 and expect the similarities between the ligands to result in only subtle changes in reaction rate. Indeed, there was no experimental reason to suppose that the Schroeder–Wrighton mechanism is not functional with the $Fe(PF_3)_x(CO)_{5-x}$ species, $x = 0$–4.

The most surprising result that has come out of this study is the fact that, although PF_3 substitution incrementally influences the isomerization, total substitution causes the isomerization to cease. There is absolutely nothing in the known chemistry of $Fe(PF_3)_5$ as compared to the $Fe(PF_3)_x(CO)_{5-x}$ species that would have led us to expect this radical difference. There is abundant evidence to make us believe that the photolysis of the M–PF_3 bond is qualitatively similar to that of the M–CO bond. This statement can be made for a number of reasons. (1) Although the main spectral absorption band moves incrementally toward higher energy as the PF_3 substitution increases, there is still strong absorption[15] in the 400–450-nm region used. Even without light filtration no reaction occurs. (2) Kruck[16] has photochemically made a number of ligand-substitution complexes, $LFe(PF_3)_4$, from $Fe(PF_3)_5$ and a donor. We have also done so. (3) Both mass spectral and NMR studies[13] on the photochemical substitution of ligands into $Fe(PF_3)_x(CO)_{5-x}$ compounds have shown that the PF_3 and CO ligands are lost in a nearly statistical fashion. (4) A solution of $(1\text{-pentene})Fe(PF_3)_4$ plus 1-pentene is photochemically quite active toward the formation of an as yet uncharacterized species (but not accompanied by isomerization of the pentene). This must clearly mean that a PF_3 group is photochemically active in $(1\text{-pentene})Fe(PF_3)_4$.

Table III. Comparison of the Photochemical Reactivity for the Isomerization of 1-Pentene[a]

compd	% 1-pentene remaining	compd	% 1-pentene remaining
$Fe(PF_3)_4CO$	4.6	$H_2Fe(PF_3)_3CO$	16.6
$Fe(PF_3)_5$	98.5	$H_2Fe(PF_3)_4$	99.2

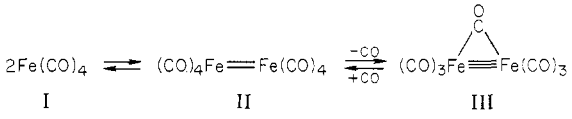
[a] Samples irradiated simultaneously at ambient temperature for 10.0 h by using unfiltered medium-pressure mercury light.

The isomerization behavior of the iron species with a CO ligand attached in contrast to $Fe(PF_3)_5$ suggests a uniqueness about CO as a ligand and implies that it possesses greater importance than a mere photosubstitutable ligand. If one concludes the carbonyl group plays an indispensable role in the photochemical isomerization of olefins, one must look for a difference between the ligands CO and PF_3 that is more than just a subtle qualitative difference. In most respects, differences are only subtle.[17] We assume that both ligands maintain their integrity and that, for instance, the P–F bonds are not specifically involved. The only significant difference of which we are currently aware is the ability of CO to act as a bridging ligand for metal atoms and the evident inability of PF_3 to do so. Not only are no PF_3-bridged compounds known, but PF_3 appears to destabilize polynuclear compounds. For instance, whereas $Fe(CO)_5$ readily forms $Fe_2(CO)_9$ upon photolysis, the individual $Fe(PF_3)_x(CO)_{5-x}$ species do not form the corresponding species as isolable compounds.

To probe further the lack of reactivity of the fully PF_3-substituted species, we carried out a parallel series of experiments with use of (1) $H_2Fe(PF_3)_4$ and (2) $H_2Fe(PF_3)_3(CO)$ in 1-pentene.[18] To test most severely the lack of reactivity of the catalyst precursor lacking a carbonyl, we carried out these experiments with use of unfiltered radiation. The results appear in Table III and once again show that the carbonyl ligand is essential to the isomerization reaction.

Thermal isomerization was studied by experiments carried out at elevated temperatures in the dark. Since the results of these experiments are reported more fully elsewhere,[15,18] only the salient points are reviewed here. While $Fe(PF_3)_5$ is not a successful isomerization catalyst precursor photochemically, at 285 °C in the dark it does produce conversion to the internal isomers; only 20.8% of the original 1-pentene remains after 24 h.

Koerner von Gustorf et al.[19] have proposed a labile, multiply bonded, carbonyl-bridged iron species to explain the behavior of $Fe(CO)_4$ in solution. They postulate



I II III

The $Fe_2(CO)_8$ dimer, II, has been observed in matrix-isolation studies.[20] A cyclobutadiene species related to III has been isolated; its proposed structure is[19]

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(13) Trifluorophosphine substitution does not always reduce the catalytic properties of metal carbonyls. In attempts photochemically to substitute tetramethylallene (Clark, R. J., unpublished results) into various $Fe(PF_3)_x(CO)_{5-x}$ species, two types of complexes are formed. One series is the simple substituted $(\text{tetramethylallene})Fe(PF_3)_x(CO)_{4-x}$ system and the other species are the isomerized $(2,4\text{-dimethyl-1,3-pentadiene})Fe(PF_3)_x(CO)_{3-x}$ compounds. As the PF_3 content of the starting iron compound increases, the rate of ligand isomerization increases so much that the butadiene complexes are formed exclusively.

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(16) Kruck, T.; Knoll, L. *Chem. Ber.* **1973**, *106*, 3578–3587.

(17) For instance, the vibrational stretching frequencies and their associated force constants and the fluorine NMR chemical shifts change only slightly as the degree of trifluorophosphine substitution changes.

(18) Clark, R. J.; Swartz, G. L.; George, H. A. "Fundamental Research in Homogeneous Catalysis"; Tsutsui, M., Ed.; Plenum Press: New York, 1979; p 835.

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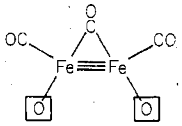

Multiply bonded carbonyl-bridged species have been studied by Ginley, Bock, and Wrighton.[21] Mechanistically a labile, multiply bonded, bridged dimeric iron species as the active catalytic intermediate is consistent with our photochemical data.

We have demonstrated that (1-pentene)Fe$(PF_3)_4$ has a PF_3 group that is photochemically active but that isomerization does not occur and that $Fe(PF_3)_5$ and $H_2Fe(PF_3)_4$ induce isomerization at elevated temperatures in the dark, but not photochemically. Thus we conclude that the higher PF_3-substituted iron carbonyls do not react by the Schroeder–Wrighton mechanism. Experimental evidence demonstrates the need for CO to generate photochemically a catalytically active species; we suggest that its function is formation of a bridged diiron species. A detailed mechanism for this process is proposesd elsewhere.[15]

Direct observation of a bridged species has been attempted. Analysis of reaction mixtures for a bridging carbonyl by infrared spectroscopy, however, is vitiated by the presence, in the spectral region of interest, of alkene bands which shift as the reaction proceeds. While the duration of the dark reaction following photolysis shows that the catalytic species has an adequate lifetime to be observed, failure to achieve its conclusive detection is likely due to its low concentration.

We plan to seek evidence for the carbonyl-bridged polynuclear species in a study of (olefin)Fe$(PF_3)_x(CO)_{4-x}$ compounds. A study of the chemistry of $Fe(PF_3)_x(CO)_{5-x}$ species in low-temperature matrices, a collaborative project with Turner and Poliakoff, has recently begun.

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Registry No. $Fe(CO)_5$, 13463-40-6; *ax*-$Fe(CO)_4PF_3$, 53368-95-9; *eq*-$Fe(CO)_4PF_3$, 35739-13-0; *trans*-$Fe(CO)_3(PF_3)_2$, 17594-22-8; *cis*-$Fe(CO)_3(PF_3)_2$, 17594-23-9; *vic*-$Fe(CO)_3(PF_3)_2$, 53275-22-2; *trans*-$Fe(CO)_2(PF_3)_3$, 17594-25-1; *cis*-$Fe(CO)_2(PF_3)_3$, 17594-26-2; *vic*-$Fe(CO)_2(PF_3)_3$, 53275-23-3; *eq*-$Fe(CO)(PF_3)_4$, 17594-29-5; *ax*-$Fe(CO)(PF_3)_4$, 17594-28-4; $Fe(PF_3)_5$, 13815-34-4; 1-pentene, 109-67-1; *cis*-2-pentene, 627-20-3; *trans*-2-pentene, 646-04-8; $H_2Fe(PF_3)_3CO$, 72883-57-9; $H_2Fe(PF_3)_4$, 31869-56-4.

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Unsymmetrical Bis-Phosphorus Ligands. 13. Bis(*tert*-butylphosphino)(diphenylphosphino)methane and Some Derivatives[1]

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Unsymmetrical bis(tertiary phosphine) ligands of the type $Ph_2PCH_2PR^1R^2$, where R^1 = Ph and R^2 = Me and *i*-Pr and where $R^1 = R^2$ = Me and *i*-Pr, along with the derivative compounds $Ph_2P(S)CH_2PR^1R^2$, $Ph_2P(S)CH_2P(S)PR^1R^2$, $[Ph_2PCH_2Pr^1R^2]M(CO)_4$, and $[Ph_2P(S)CH_2Pr^1R^2]M(CO)_4$, where M = Cr, Mo, or W, have been reported previously.[3,4] These compounds have proved interesting from the viewpoint of nuclear magnetic resonance (NMR) studies, especially with regard to phosphorus–phosphorus spin coupling and the phosphorus chelate shift effect.[5,6] The analogous compounds reported here, viz., $Ph_2PCH_2P(t\text{-}Bu)_2$ and its derivatives and $Ph_2P(S)CH_2P(s\text{-}Bu)_2$, extend and complement the previous studies.

The monosulfide, $Ph_2P(S)CH_2P(t\text{-}Bu)_2$ was prepared in 43% purified yield from $Ph_2P(S)CH_2Li$[7] and $(t\text{-}Bu)_2PCl$ according to the reaction scheme shown by eq 1 and 2. In order to reduce the extent of side reactions,[3] we placed phosphinous chloride in the reaction flask, and the lithium reagent was added dropwise. The disulfide $Ph_2P(S)CH_2P(S)(t\text{-}Bu)_2$ was prepared from the monosulfide by heating with elemental sulfur in benzene. The bis(tertiary phosphine) $Ph_2PCH_2P(t\text{-}Bu)_2$ was prepared as a viscous colorless oil in 75% yield from the monosulfide by reduction with Si_2Cl_6 in benzene. Quaternization of the monosulfide with methyl bromide produced the phosphonium salt $[Ph_2P(S)CH_2P(t\text{-}Bu)_2Me]Br$. Coordination reactions of the monosulfide to form a five-membered chelate ring and of the bis(tertiary phosphine) to form a four-membered chelate ring, by displacement of 2 CO's from $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$, were carried out in a straightforward manner by direct reaction at ca. 100 °C. Apparently, the large steric bulk of the two *tert*-butyl groups of phosphorus did not materially affect its coordination ability, even when it was necessary to form a strained four-membered chelate ring. All of the types of reactions described above were also observed earlier with the methyl and isopropyl analogues.[3] However, the sulfur-transfer reaction (eq 3),[8] which is quite clean and can be used synthetically in the case of the methyl and isopropyl analogues, did not occur cleanly with $Ph_2P(S)CH_2P(t\text{-}Bu)_2$. Phosphorus-31 NMR evidence did indicate that some sulfur transfer had taken place with the *tert*-butyl compound, but the resulting reaction mixture was complex, and the products were not isolated or identified. It is likely that the steric effect of the *tert*-butyl groups plays an inhibitory role in this reaction.

$$Ph_3PS + CH_3Li \rightarrow Ph_2P(S)CH_2Li + C_6H_6 \qquad (1)$$

$$(t\text{-}Bu)_2PCl + Ph_2P(S)CH_2Li \rightarrow Ph_2P(S)CH_2P(t\text{-}Bu)_2 + LiCl \qquad (2)$$

$$Ph_2P(S)CH_2PR^1R^2 \xrightarrow{140\text{–}160\ ^\circ C} Ph_2PCH_2P(S)R^1R^2 \qquad (3)$$

The synthesis of $Ph_2P(S)CH_2P(s\text{-}Bu)_2$ led to a mixture of stereoisomers which exhibited three pairs of overlapping doublets in the ^{31}P NMR spectrum. Each diastereomer gives an AX spectrum with only a small degree of second-order character, i.e., a pair of doublets, the high-frequency doublet arising from P(V) in each case.

The ^{31}P NMR data are as follows: isomer A, $\delta(Ph_2PS)$ 42.0, $\delta(P(s\text{-}Bu)_2)$ −16.7, (J_{PP} = 78.7 Hz, relative intensity 0.43; isomer B, $\delta(Ph_2PS)$ 41.7, $\delta(P(s\text{-}Bu)_2)$ −15.9 (J_{PP} = 76.3,

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