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Sulfur Dioxide Complexes of Iron(0): [Fe(L)$_2$(CO)$_2$(SO$_2$)] (L = P(III) Ligand). Isomerism and the Structures of [Fe(P(OPh)$_3$)$_2$(CO)$_2$(SO$_2$)] and [Fe(P(OC$_6$H$_4$Me-*o*)$_3$)$_2$(CO)$_2$(SO$_2$)]

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A series of air-stable [Fe(L)$_2$(CO)$_2$(SO$_2$)] complexes (L = P(III) ligand) have been prepared either from [Fe(L)$_2$(CO)$_3$] by photolysis and subsequent reaction with SO$_2$ when L is a triaryl phosphite or from [Fe(L)$_2$(CO)$_2$(CS$_2$)] by the thermal or photolytic displacement of CS$_2$ by SO$_2$. Their IR spectra are reported and absorption bands due to ν(CO) and ν(SO$_2$) vibrations are assigned. They show that there are two isomeric forms of these complexes, A and B, and the structures of one of each have been determined by X-ray diffraction studies. In both there is trigonal-bipyramidal coordination about Fe with a planar η^1(S)-SO$_2$ ligand coordinated equatorially so that the SO$_2$ plane lies ca. perpendicular to the equatorial plane of the complex. However, in [Fe(P(OPh)$_3$)$_2$(CO)$_2$(SO$_2$)] (an isomer A) the two phosphite ligands are axially coordinated, while in [Fe(P(OC$_6$H$_4$Me-*o*)$_3$)$_2$(CO)$_2$(SO$_2$)] (an isomer B) they are equatorial. In the solid state all of the complexes adopt the A configuration except when L = (*o*-ClC$_6$H$_4$O)$_3$P, (*o*-MeC$_6$H$_4$O)$_3$P, or Ph(*o*-MeC$_6$H$_4$O)$_2$P. In solution the complexes are found solely as A when L = (*p*-ClC$_6$H$_4$O)$_3$P, (*i*-PrO)$_3$P, Ph(*i*-PrO)$_2$P, Ph(MeO)$_2$P, Ph$_2$(PhO)P, Ph$_2$(MeO)P, Ph$_2$MeP, and Ph$_3$P. When L = (*o*-ClC$_6$H$_4$O)$_3$P, only B is observed. However there is a solvent-dependent equilibrium mixture of A and B when L = (*o*-MeC$_6$H$_4$O)$_3$P, Ph(*o*-MeC$_6$H$_4$O)$_2$P, (*m*-MeC$_6$H$_4$O)$_3$P, (*p*-MeC$_6$H$_4$O)$_3$P, (PhO)$_3$P, Ph(PhO)$_2$P, and Ph$_2$(*o*-MeC$_6$H$_4$O)P with the proportion of B declining along this series in a particular solvent. It is proposed that this equilibrium is largely a consequence of steric effects. A is destabilized by steric interactions between the SO$_2$ ligand and the ortho-H atoms of the axial L ligands, and B is destabilized by L–L interactions. Electronic factors also play their limited part and arise from the nature of the bonding between all three equatorial ligands and Fe. The structures of two of the complexes were solved by the heavy-atom method and refined by least-squares procedures. [Fe(P(OPh)$_3$)$_2$(CO)$_2$(SO$_2$)] crystals (an example of isomer A) were triclinic, space group *P*1, or *P*$\bar{1}$, with *a* = 11.027 (5) Å, *b* = 11.374 (5) Å, *c* = 15.238 (8) Å, α = 88.3 (1)°, β = 97.7 (1)°, γ = 108.6 (1)°, and *Z* = 2, and the structure was refined to *R* = 0.083 for 2437 non-zero unique photographic reflections. [Fe(P(OC$_6$H$_4$Me-*o*)$_3$)$_2$(CO)$_2$(SO$_2$)] crystals (an example of isomer B) were monoclinic, space group *Cc* or *C*2/*c*, with *a* = 19.873 (11) Å, *b* = 10.725 (5) Å, *c* = 20.798 (11) Å, β = 100.7 (1)°, and *Z* = 4, and the structure was refined to *R* = 0.088 for 1309 non-zero unique photographic reflections.

Introduction

We have shown that the η^2-CS$_2$ ligand in the readily available [Fe(L)$_2$(CO)$_2$(η^2-CS$_2$)] complexes (L is a P(III) ligand) is replaced by SO$_2$.[2] This provides a reasonable route to the otherwise relatively inaccesible [Fe(L)$_2$(CO)$_2$(SO$_2$)] derivatives. We have also reported that those SO$_2$ complexes where L is a triaryl phosphite ligand (ArO)$_3$P only may be obtained from photolysis of [Fe(P(OAr)$_3$)$_2$(CO)$_3$] to "[Fe(P-(OAr)$_3$)$_2$(CO)$_2$]" followed by their reaction with SO$_2$.[3] Here we describe a number of [Fe(L)$_2$(CO)$_2$(SO$_2$)] derivatives, their rather limited ligand-exchange reactions, their isomerism, and the structures of two of them, one of each isomer type. We discuss briefly the bonding in the two isomers and their mode of interconversion. A preliminary communication has been published.[4]

The field of metal–SO$_2$ complexes has been reviewed twice recently.[5,6] However, of direct relevance to our work are the preparations of [Fe(PEt$_3$)$_2$(CO)$_2$(SO$_2$)][7] and [Fe(PPh$_3$)$_2$-(CO)$_2$(SO$_2$)][8] by photochemical techniques and of [Fe$_2$-(CO)$_8$(μ-SO$_2$)] from [Fe$_2$(CO)$_9$] and SO$_2$[9] and the reaction of [Pt(PPh$_3$)$_2$(η^2-CS$_2$)] with SO$_2$. This last reaction does not result in CS$_2$/SO$_2$ interchange; instead it gives [Pt(PPh$_3$)$_2$-(S$_2$CO)].[10]

Experimental Section

Literature methods or modifications of them were used to prepare most of the phosphorus(III) ligands listed in Table I,[11] [Fe$_2$(CO)$_9$],[12] [Fe(P(OAr)$_3$)$_2$(CO)$_3$] (Ar = Ph, *o*-ClC$_6$H$_4$, *p*-ClC$_6$H$_4$),[13] and [Fe-(L)$_2$(CO)$_2$(η^2-CS$_2$)].[2] Other chemicals were purchased.

Unless it is stated otherwise, all reactions were carried out at room temperature under an atmosphere of nitrogen in solvents that had been dried and deoxygenated by heating them to reflux over magnesium metal (for alcohols) or calcium hdyride (all other solvents) and distilling them prior to use. Tetrahydrofuran was further purified by distillation from sodium and benzophenone.

IR spectra were run on a Perkin-Elmer 337 spectrometer equipped with a Hitachi Perkin-Elmer readout recorder. They were calibrated with polystyrene except in the 1900–2100-cm^{-1} region, where DCl was used.[15]

Mass spectra were run on a VG 70/70 M mass spectrometer. They showed only ion peaks due to the ligand and will not be discussed further.

Analyses were carried out in the Analytical Laboratory of University College, Dublin, Ireland.

The melting points, analyses, and IR spectra of the [Fe(L)$_2$(C-O)$_2$(SO$_2$)] complexes are summarized in Table I.

Preparation of [Fe(P(OAr)$_3$)$_2$(CO)$_2$(SO$_2$)] from [Fe(P(OAr)$_3$)$_2$-(CO)$_3$] (Ar = *o*- or *p*-ClC$_6$H$_4$). The photolysis of a solution of [Fe(P(OAr)$_3$)$_2$(CO)$_3$] (1 g, Ar = *p*-ClC$_6$H$_4$) in benzene (100 mL) was carried out at 5–10 °C with a Philips HPR 125-W lamp with nitrogen gas bubbling through the reaction mixture. All of the reactant had disappeared after 4 h, so the lamp was switched off and SO$_2$ gas

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Table I. Melting Points, Analyses, and IR Spectra of [Fe(L)₂(CO)₂(SO₂)] Complexes

L	mp, °C	anal.[a] % C	% H	% S	ν(CO) (CS₂ soln)[c]	ν(CO) (CS₂ soln)	ν(CO) (IR spectra[b])	ν(SO₂)sym	ν(SO₂)asym
(o-ClC₆H₄O)₃P	127–130	45.2 (45.5)	2.6 (2.4)	3.6 (3.2)	2011 (10)	2013 (6.0), 1958 (10)	1980 (sh), 2011 (vs)	1100	1219
(p-ClC₆H₄O)₃P	151–156	45.6 (45.5)	2.2 (2.4)	2.8 (3.2)		2010 (6.8), 1954 (10)	1967 (vs), 1974 (m), 2019 (s)	1076, 1086	1223
(PhO)₃P	130–134	57.3 (57.3)	4.0 (3.7)	5.1 (4.0)	1997 (2.1)	2006 (6.9), 1952 (10)	1954 (vs), 2013 (7.9)	1085	1245
(o-MeC₆H₄O)₃P	107–109	60.2 (60.0)	4.6 (4.8)	4.0 (3.6)	1998 (10)	2012 (6.5), 1955 (10)	1989 (vs)	1108	1265
(m-MeC₆H₄O)₃P	75–78	60.4 (60.0)	4.6 (4.8)	4.1 (3.6)	1996 (4.4)	2011 (6.0), 1955 (5.3)	1942 (vs), 1993 (sh), 2006 (m)	1090	
(p-MeC₆H₄O)₃P	131–134	60.3 (60.0)	4.7 (4.8)	4.0 (3.6)	1995 (2.0)	1995 (3.3), 1934 (10)	1939 (m), 1965 (vs), 2018 (s)	1080	1232
(i-PrO)₃P	105–108	40.5 (40.5)	7.2 (7.1)	5.9 (5.4)		2005 (7.7), 1948 (10)	1929 (m), 1946 (vs), 1993 (m), 2004 (s)	1083	1223
Ph(PhO)₂P	133–138	59.5 (59.7)	3.8 (3.9)	4.6 (4.6)	1985 (0.8)	2001 (7.2), 1946 (10)	1947 (vs), 2004 (m)	1110	1248
Ph(o-MeC₆H₄O)₂P	170 dec	61.7 (61.5)	4.6 (4.6)	4.3 (3.9)	1980 (4.1)	1994 (7.2), 1938 (10)	1944 (sh), 1975 (vs)	1084, 1110	1220, 1260
Ph(MeO)₂P	139–142	41.9 (41.9)	4.2 (4.3)	6.0 (6.2)		1991 (8.4), 1934 (10)	1913 (sh), 1940 (vs), 1950 (sh), 1995 (s)	1078	1225
Ph(i-PrO)₂P	137–139	49.8 (49.7)	6.4 (6.1)	5.2 (5.1)		1989 (5.4), 1938 (10)	1928 (vs), 1986 (m)	1079	1226
Ph₂(PhO)P	150 dec	62.3 (62.3)	4.3 (4.1)	4.9 (4.4)		1987 (5.0), 1930 (10)	1946 (vs), 1992 (m)	1083	1230
Ph₂(o-MeC₆H₄O)P	154–156	61.0 (63.2)	4.6 (4.5)	5.3 (6.0)		1983 (5.0), 1927 (10), 2003 (6.6)	1926 (vs), 1987 (m)	1081	1231
Ph₂(McO)P	135–138	55.5 (55.3)	4.5 (4.5)			1988 (5.1), 1918 (10)	1889 (sh), 1919 (vs), 1960 (sh), 1979 (m)		
Ph₂McP	135 dec	57.9 (58.3)	5.8 (4.5)	5.2 (4.6)		1974 (4.9), 1916 (10)	1903 (vs), 1970 (m)	1080, 1096	1229
Ph₃P	100 dec	65.2 (65.1)	4.5 (4.3)				1020 (vs), 1982 (s)	1068	1201, 1205

[a] Found (calculated). [b] Measured in KBr disks unless stated otherwise. Peak positions are given in cm⁻¹, with relative peak heights in parentheses. Abbreviations: vs = very strong, s = strong, m = medium, sh = shoulder. [c] Absorption band due to isomer B in CS₂ solution.

Table II. Effect of Solvent on the IR Spectra[a] (1900–2100-cm⁻¹ Region) of [Fe(L)₂(CO)₂(SO₂)] Complexes

	solvent			
L	CS₂	CHCl₃	MeCN	m-cresol
(PhO)₃P	1954 (10)	1959 (10)	1960 (10)	1969 (10)
	1997 (2.1)	2001 (5.6)	1999 (6.3)	2004 (7.5)
	2010 (6.8)	2016 (6.5)	2016 (6.4)	2022 (6.5)
(o-MeC₆H₄O)₃P	1952 (10)	1955 (10)	1956 (10)	1961 (10)
	1998 (10)	1995 (39)	1992 (37)	1998 (65)
	2006 (6.9)	2001 (7.3)	2030 (6.4)	
Ph(PhO)₂P	1948 (10)	1952 (10)	1954 (10)	1952 (10)
	1985 (0.8)	1985 (3.0)	1985 (3.7)	1985 (4.2)
	2005 (7.7)	2010 (7.5)	2008 (6.6)	2010 (7.9)
Ph(o-MeC₆H₄O)₂P	1946 (10)	1952 (10)	1949 (10)	1954 (10)
	1980 (4.1)	1985 (28)	1981 (38)	1990 (88)
	2001 (7.2)	2009 (6.9)	2001 (5.5)	2003 (sh)
Ph₂(o-MeC₆H₄O)P	1930 (10)	1935 (10)	1934 (10)	1946 (10)
		1969 (2.6)	1971 (3.5)	1984 (5.7)
	1987 (5.0)	1991 (5.2)	1992 (5.2)	2001 (6.7)

[a] Peak positions are given in cm⁻¹, with relative peak heights in parentheses.

bubbled through the reaction mixture for 10 min. The deep orange solution was filtered, the solvent was removed at reduced pressure, and the residue was recrystallized from tetrahydrofuran. The yield of orange crystals of [Fe(P(OC₆H₄Cl-p)₃)₂(CO)₂(SO₂)] was 55%.

The reaction was repeated with [Fe(P(OC₆H₄Cl-o)₃)₂(CO)₃], but after 8 h of irradiation only ca. 30% of this had been consumed. However, the lamp was switched off at this stage and SO₂ bubbled through the reaction mixture. Removal of the solvent gave an orange solid, which was recrystallized three times from tetrahydrofuran-methanol mixtures. The yield of [Fe(P(OC₆H₄Cl-o)₃)₂(CO)₂(SO₂)] was only 10%.

Preparation of [Fe(L)₂(CO)₂(SO₂)] from [Fe(L)₂(CO)₂(η²-CS₂)]. A stream of SO₂ gas was passed through a cooled solution (0–10 °C) of [Fe(L)₂(CO)₂(η²-CS₂)] (1 g) in tetrahydrofuran (50 mL) while the mixture was irradiated with a Philips HPR 125-W lamp. When L = Ph₃P, CH₂Cl₂ was used as the reaction solvent. When the reactions were complete (1–8 h), the mixtures were filtered and the solvents removed at reduced pressure. The residues were recrystallized from tetrahydrofuran–methanol mixtures except when L = (i-PrO)₃P, for which pentane was used. The yields of orange [Fe(L)₂(CO)₂(SO₂)] were generally ca. 50% but rose to 63% when L = (PhO)₃P and dropped to 38% when L = Ph₃P.

These reactions take place in the dark but are much slower. When L = o- or p-(ClC₆H₄O)₃P, these reactions were very slow.

Ligand-Exchange Reactions. A solution of [Fe(P(OPh)₃)₂(CO)₂(SO₂)] (1 g) and Ph₃P (2 g) in benzene (50 mL) was heated to reflux. After 30 min the only SO₂-containing species present was [Fe(PPh₃)₂(CO)₂(SO₂)], which was isolated as described above (yield 65%).

If Ph₃P was replaced by Ph₂(o-MeC₆H₄O)P (2 mL), a similar reaction took place but no pure product could be isolated.

Structure Analysis. Crystal data for I: C₃₈H₃₀O₁₀P₂SFe, M_r = 796.5, triclinic, a = 11.027 (5) Å, b = 11.374 (5) Å, c = 15.328 (8) Å, α = 88.3 (1)°, β = 97.7 (1)°, γ = 108.6 (1)°, V = 1805.9 Å³, D_{measd} = 1.45 Mg m⁻³ (by flotation), Z = 2, D_{calcd} = 1.464 Mg m⁻³, F(000) = 820, μ(Mo Kα) = 6.3 cm⁻¹, space group P1 (No. 1) or P1̄ (No. 2). Crystal data for II: C₄₄H₄₂O₁₀P₂SFe, M_r = 880.7, monoclinic, a = 19.873 (11) Å, b = 10.725 (5) Å, c = 20.798 (11) Å, β = 100.7 (1)°, V = 4355.4 Å³, D_{measd} = 1.35 Mg m⁻³ (by flotation), Z = 4, D_{calcd} = 1.343 Mg m⁻³, F(000) = 1832, μ(Mo Kα) = 5.3 cm⁻¹, systematic absences hkl if h + k ≠ 2n and h0l if l ≠ 2n, space group Cc (No. 9) or C2/c (No. 15).

Cell parameters were determined from precession photographs with Mo Kα radiation of λ = 0.71069 Å. Intensities were estimated visually for (0–3)kl, hk(0–4), and layers 0–4 about [101] for I and (0–4)kl, hk(0–6), and layers 0–4 about [101] for II. They were corrected for Lorentz and polarization effects but not for absorption or extinction. A total of 2437 non-zero unique reflections were obtained for I and 1309 for II. The observed structure factors were placed on a common scale by internal correlation. Neutral-atom scattering factors were taken from ref 16 and were not corrected for anomalous dispersion.
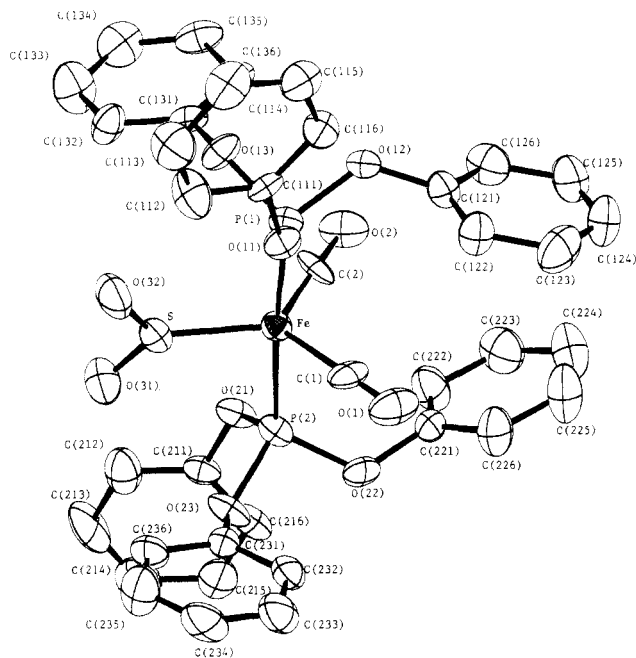
Figure 1. Perspective drawing of [Fe(P(OPh)₃)₂(CO)₂(SO₂)] (I) with the atom-labeling scheme. Thermal ellipsoids are drawn to include 35% probability.
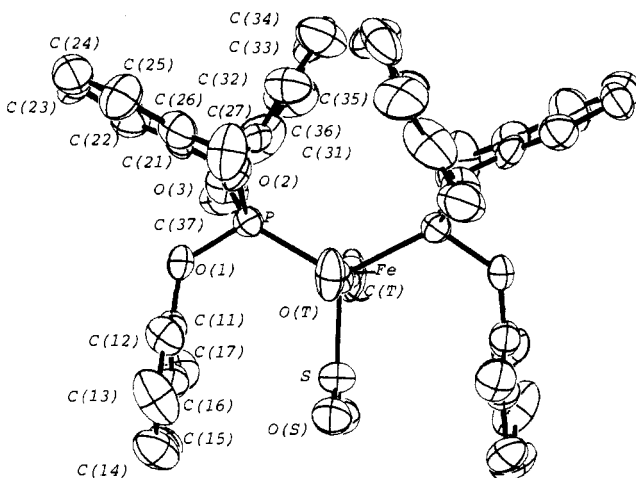
Figure 2. Perspective drawing of [Fe(P(OC₆H₄Me-*o*)₃)₂(CO)₂(SO₂)] (II) with the atom-labeling scheme. Thermal ellipsoids are drawn to include 35% probability.

All calculations were carried out on a UNIVAC 1106 computer with programs written by F.S.S.

The structures were solved by the heavy-atom method, the centrosymmetric space groups being adopted for both. The Patterson synthesis for II indicated the presence of a crystallographic twofold axis for the Fe, P, and S atom vectors. Refinements were carried out by least-squares calculations in which $\sum w\Delta^2$ values were minimized. The weights w for each reflection were initially unity and in the final cycles given by $w = (10.0 + 0.6|F_o| + 0.01|F_o|^2)^{-1}$ for I and $w = (12.5 + 1.2|F_o| + 0.008|F_o|^2)^{-1}$ for II, schemes chosen such that the average values of $w\Delta^2$ for ranges of increasing F_o were almost constant. Approximate hydrogen atom positions were obtained from difference maps and they were optimized with C–H assumed to be 1.0 Å. The contributions of these atoms were included in the calculations, but their parameters were not refined. Anisotropic refinements were carried out with eight block matrices for I and a full matrix for II. A reflection was rejected from a least-squares cycle if $|F_c| < 0.2|F_o|$, and the refinements were terminated when the maximum shift in any parameter was $<0.2\sigma$. As a consequence four
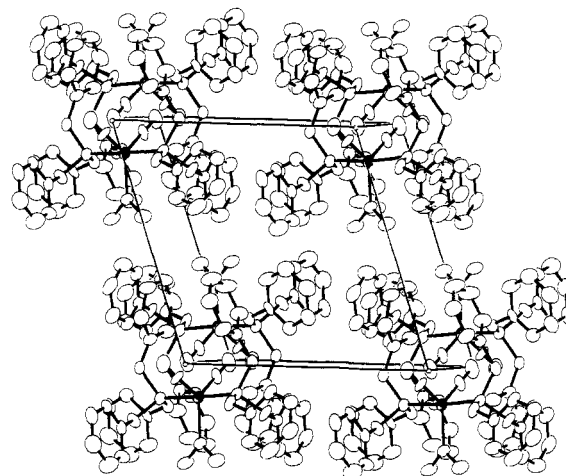
Figure 3. Packing of the [Fe(P(OPh)₃)₂(CO)₂(SO₂)] molecules in the unit cell.
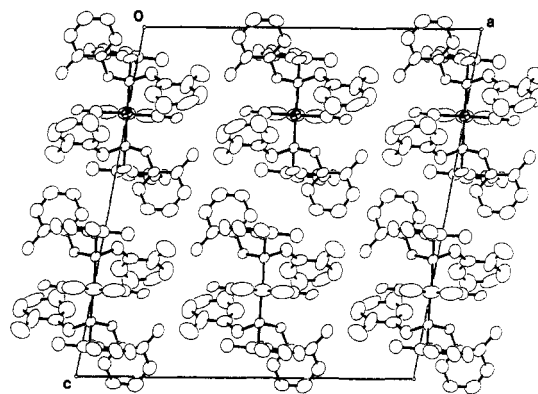
Figure 4. Packing of the [Fe(P(OC₆H₄Me-*o*)₃)₂(CO)₂(SO₂)] molecules in the unit cell.

reflections were omitted from the final least-squares cycle for I and three for II. The final R values were 0.083 for I and 0.088 for II while $R' = (\sum w\Delta^2/\sum w|F_o|^2)^{1/2}$ values were 0.115 for I and 0.121 for II. The final difference maps showed no electron densities $>|0.7|$ e Å⁻³ for I and $>|0.5|$ e Å⁻³ for II.

Molecular structures and atom labeling are shown in Figures 1 and 2,[17] and the packing of the molecules in the unit cells are shown in Figures 3 and 4. Final atom coordinates are listed in Tables III and IV. Selected bond lengths and angles are contained in Tables V and VI and the important ones compared in Table VII. The following have been deposited as supplementary material: Table VIII, nonbonding interatomic contact distances; Tables IX and X, observed and calculated structure factors; Tables XI and XII, final atomic anisotropic thermal parameters; Tables XIII and XIV, atomic parameters for hydrogen atoms; Tables XV and XVI, least-squares planes data.

Results and Discussion

The [Fe(L)₂(CO)₂(SO₂)] complexes that we have prepared (Table I) are yellow crystalline solids soluble in organic solvents. They are quite stable in air when solid, but if L is a trialkyl phosphite, they tend to discolor. This behavior is quite different from that of [Ru(L)₂(CO)₂(SO₂)] complexes, which are air sensitive and oxidize readily to [Ru(PR₃)₂(CO)₂-(SO₄)].[8]

We have used two routes to prepare the complexes, and where both have been used they give the same product. One is limited to derivatives of triaryl phosphites, (ArO)₃P. UV photolysis of [Fe(P(OAr)₃)₂(CO)₃] results in CO loss and the

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Table III. Final Atomic Coordinates (Fractional, ×10³) with Estimated Standard Deviations in Parentheses, for [Fe(P(OPh)₃)₂(CO)₂(SO₂)] (I)

	x/a	y/b	z/c
Fe	37.0 (2)	142.8 (2)	249.2 (1)
S	85.4 (4)	332.4 (3)	246.8 (3)
P(1)	212.2 (4)	150.8 (3)	334.9 (2)
P(2)	−142.7 (4)	121.4 (3)	162.7 (2)
C(1)	−51 (1)	53 (1)	332 (1)
C(2)	83 (1)	60 (1)	170 (1)
O(31)	26 (1)	398 (1)	181 (1)
O(32)	183 (1)	415 (1)	310 (1)
O(1)	−109 (1)	−5 (1)	382 (1)
O(2)	113 (1)	3 (1)	122 (1)
O(11)	211 (1)	183 (1)	435 (1)
O(12)	259 (1)	30 (1)	339 (1)
O(13)	346 (1)	248 (1)	318 (1)
O(21)	−124 (1)	157 (1)	63 (1)
O(22)	−251 (1)	−14 (1)	158 (1)
O(23)	−235 (1)	198 (1)	179 (1)
C(111)	320 (1)	227 (1)	499 (1)
C(112)	354 (2)	350 (1)	524 (1)
C(113)	453 (2)	395 (2)	587 (1)
C(114)	527 (2)	320 (2)	626 (1)
C(115)	490 (2)	199 (1)	600 (1)
C(116)	388 (2)	150 (1)	536 (1)
C(121)	182 (1)	−92 (1)	350 (1)
C(122)	120 (2)	−124 (1)	423 (1)
C(123)	56 (2)	−250 (2)	434 (1)
C(124)	59 (2)	−337 (1)	375 (2)
C(125)	119 (2)	−304 (1)	301 (1)
C(126)	180 (2)	−180 (1)	288 (1)
C(131)	390 (1)	277 (1)	237 (1)
C(132)	417 (1)	396 (1)	208 (1)
C(133)	469 (2)	429 (2)	131 (1)
C(134)	497 (2)	344 (2)	82 (1)
C(135)	474 (1)	228 (2)	111 (1)
C(136)	416 (1)	189 (1)	188 (1)
C(211)	−210 (1)	194 (1)	1 (1)
C(212)	−177 (2)	310 (1)	−28 (1)
C(213)	−262 (3)	345 (2)	−92 (1)
C(214)	−376 (2)	261 (2)	−125 (1)
C(215)	−408 (2)	143 (1)	−96 (1)
C(216)	−323 (2)	106 (1)	−33 (1)
C(221)	−222 (1)	−126 (1)	9 (1)
C(222)	−187 (2)	−148 (1)	18 (1)
C(223)	−169 (2)	−262 (2)	59 (1)
C(224)	−189 (2)	−352 (2)	120 (2)
C(225)	−227 (2)	−322 (1)	200 (1)
C(226)	−245 (2)	−210 (1)	212 (1)
C(231)	−259 (1)	228 (1)	260 (1)
C(232)	−322 (1)	148 (1)	316 (1)
C(233)	−357 (2)	179 (1)	392 (1)
C(234)	−327 (2)	300 (1)	411 (1)
C(235)	−260 (2)	387 (1)	358 (1)
C(236)	−229 (1)	351 (1)	280 (1)

Table IV. Final Atomic Coordinates (Fractional, ×10⁴), with Estimated Standard Deviations in Parentheses, for [Fe(P(OC₆H₄Me-o)₃)₂(CO)₂(SO₂)] (II)

	x/a	y/b	z/c
Fe	0	880 (2)	2500
S	0	−1036 (6)	2500
P	124 (2)	1840 (3)	27 (2)
C(T)	919 (10)	910 (16)	2548 (9)
O(T)	1491 (6)	901 (13)	2603 (6)
O(S)	610 (9)	−1765 (12)	2540 (6)
O(1)	226 (5)	1031 (9)	4089 (5)
O(2)	778 (4)	2742 (8)	3557 (5)
O(3)	−481 (5)	2579 (11)	3666 (6)
C(11)	484 (8)	−211 (14)	4155 (8)
C(12)	1186 (7)	−358 (15)	4216 (9)
C(13)	1467 (10)	−1515 (26)	4287 (12)
C(14)	1041 (13)	−2502 (19)	4270 (12)
C(15)	362 (12)	−2395 (17)	4213 (10)
C(16)	52 (9)	−1216 (16)	4143 (9)
C(17)	−707 (9)	−999 (17)	4073 (10)
C(21)	1112 (8)	3303 (13)	4144 (8)
C(22)	776 (9)	3697 (15)	4628 (10)
C(23)	1133 (11)	4316 (16)	5197 (9)
C(24)	1807 (13)	4517 (18)	5223 (12)
C(25)	2138 (10)	4114 (21)	4733 (13)
C(26)	1806 (9)	3526 (15)	4155 (11)
C(27)	2171 (9)	3138 (23)	3658 (11)
C(31)	−922 (10)	3427 (13)	3377 (8)
C(32)	−653 (11)	4436 (19)	3082 (12)
C(33)	−1033 (14)	5356 (20)	2766 (14)
C(34)	−1730 (20)	5304 (27)	2828 (14)
C(35)	−2040 (11)	4250 (24)	3046 (14)
C(36)	−1598 (10)	3408 (23)	3353 (14)
C(37)	−1918 (13)	2320 (20)	3676 (13)

formation of "[Fe(P(OAr)₃)₂(CO)₂]", which are probably ortho-metalated species and which with SO₂ form [Fe(P(O-Ar)₃)₂(CO)₂(SO₂)].[3] As the alternatives are so slow, this is the only practical route to those complexes where Ar = p- or o-ClC₆H₄ and it too is slow for the last of these.

The second and more general route is the thermal or photochemical reaction of [Fe(L)₂(CO)₂(η²-CS₂)] with SO₂.[2] CS₂ is displaced to give [Fe(L)₂(CO)₂(SO₂)], generally in yields of ca. 50% with some [Fe(L)₂(CO)₃] as side products. The reaction times were usually short (ca. 1 h) when L was large and long (ca. 8h) when L was small. It is well-known that the phosphorus(III) ligands L in [Fe(L)₂(CO)₂(η²-CS₂)] complexes are labile, especially when they are bulky.[2,14] Therefore it seems reasonable to suggest that the replacement of CS₂ by SO₂ proceeds by a ligand L dissociative pathway, perhaps to give [Fe(L)(CO)₂(CS₂)] with the subsequent formation of [Fe(L)(CO)₂(CS₂)(SO₂)] and the displacement of CS₂ from it by free L. A possible alternative reaction pathway is associative with the formation of [Fe(L)₂(CO)₂-

(CS₂)(SO₂)] having either Fe→SO₂ or FeCS₂→SO₂ bonding. Its feasibility is a consequence of the Lewis acidity of SO₂, a property which also accounts for its facile reaction with [Ru(PPh₃)₂(CO)₃],[8] and its ability to form ligand–SO₂ bonds e.g. in [Pt(PPh₃)₂(Me)(I→SO₂)][18] and perhaps in the directly relevant reaction of [Pr(PPh₃)₂(η²-CS₂)] with SO₂, which gives [Pt(PPh₃)₂(S₂CO)] rather than [Pt(PPh₃)₂(SO₂)].

In view of the reaction of [Fe₂(CO)₉] with SO₂, which gives [Fe₂(CO)₈(μ-SO₂)],[9] we had hoped that if it were carried out in the presence of phosphorus(III) ligands, L, we might obtain other SO₂ complexes (cf. CS₂, [Fe₂(CO)₉], and L[2,14]). Unfortunately the only detectable products were [Fe(L)(CO)₄] and [Fe(L)₂(CO)₃].

Ligand Replacement Reactions. Triphenylphosphine and triphenyl phosphite ligands are very labile in their [Fe(L)₂-(CO)₂(η²-CS₂)] complexes and may be replaced readily at room temperature without loss of CS₂.[2,14] However, the same is not true for their SO₂ counterparts. Thus [Fe(P-(OPh)₃)₂(CO)₂(SO₂)] does not react with Ph₃P at 25 °C, but it does react with an excess of it in boiling benzene. After ¹/₂ h the substrate has disappeared, and [Fe(PPh₃)₂(CO)₂(SO₂)] is formed together with a variety of [Fe(L)₂(CO)₃] and some [Fe(L)(CO)₄] species containing Ph₃P or (PhO)₃P ligands or both. These increase in importance with increasing reaction times. There is IR spectroscopic evidence for an intermediate species, which may be [Fe(P(OPh)₃)(PPh₃)(CO)₂(SO₂)].

Structures of [Fe(P(OPh)₃)₂(CO)₂(SO₂)] (I) and [Fe(P-(OC₆H₄Me-o)₃)₂(CO)₂(SO₂)] (II). There are two isomeric forms of the [Fe(L)₂(CO)₂(SO₂)] complexes. X-ray diffraction studies show that in the solid state I is an example of isomer A and II is one of B. The structures of the molecules are illustrated in Figures 1 and 2 and their packing in their unit cells in Figures 3 and 4. Bond lengths and angles are given in Tables V and VI and the important ones compared in Table VII.

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Table V. Bond Lengths and Angles, with Estimated Standard Deviations in Parentheses, for [Fe(P(OPh)$_3$)$_2$(CO)$_2$(SO$_2$)] (I)

(a) Bond Lengths (Å)

Fe–P(1)	2.164 (5)	P(1)–O(13)	1.585 (9)	S–O(31)	1.447 (12)	P(2)–O(22)	1.616 (9)
Fe–S	2.051 (4)	O(11)–C(111)	1.415 (15)	S–O(32)	1.450 (12)	P(2)–O(23)	1.585 (9)
Fe–C(1)	1.792 (15)	O(12)–C(121)	1.393 (15)	C(1)–O(1)	1.130 (15)	O(21)–C(211)	1.398 (16)
Fe–C(2)	1.770 (15)	O(13)–C(131)	1.397 (16)	C(2)–O(2)	1.147 (15)	O(22)–C(221)	1.444 (16)
P(1)–O(11)	1.598 (9)	Fe–P(2)	2.180 (5)	P(2)–O(21)	1.596 (9)	O(23)–C(231)	1.384 (15)
P(1)–O(12)	1.614 (9)						

	x					
	11	12	13	21	22	23
C(x1)–C(x2)	1.37 (2)	1.37 (2)	1.36 (2)	1.33 (2)	1.33 (2)	1.35 (2)
C(x2)–C(x3)	1.33 (2)	1.40 (2)	1.37 (2)	1.40 (2)	1.39 (2)	1.40 (2)
C(x3)–C(x4)	1.43 (2)	1.36 (2)	1.37 (2)	1.36 (2)	1.36 (2)	1.34 (2)
C(x4)–C(x5)	1.36 (2)	1.37 (3)	1.34 (2)	1.35 (2)	1.44 (3)	1.35 (2)
C(x5)–C(x6)	1.37 (2)	1.38 (2)	1.42 (2)	1.40 (2)	1.37 (2)	1.40 (2)
C(x6)–C(x1)	1.39 (2)	1.39 (2)	1.39 (2)	1.38 (2)	1.38 (2)	1.36 (2)

(b) Angles (deg)

P(1)–Fe–P(2)	176.2 (2)	Fe–P(1)–O(12)	118.0 (4)	P(1)–Fe–S	92.1 (2)	Fe–P(2)–O(22)	117.0 (4)
S–Fe–C(1)	121.9 (5)	Fe–P(1)–O(13)	120.6 (4)	P(1)–Fe–C(1)	87.7 (4)	Fe–P(2)–O(23)	121.5 (4)
S–Fe–C(2)	121.2 (5)	O(11)–P(1)–O(12)	104.6 (5)	P(1)–Fe–C(2)	90.5 (5)	O(21)–P(2)–O(22)	105.3 (5)
C(1)–Fe–C(2)	116.9 (7)	O(11)–P(1)–O(13)	99.8 (5)	P(2)–Fe–S	91.7 (2)	O(21)–P(2)–O(23)	99.2 (5)
Fe–S–O(31)	123.2 (5)	O(12)–P(1)–O(13)	96.6 (5)	P(2)–Fe–C(1)	89.2 (5)	O(22)–P(2)–O(23)	96.6 (5)
Fe–S–O(32)	123.8 (5)	P(1)–O(11)–C(111)	125.7 (8)	P(2)–Fe–C(2)	88.7 (5)	P(2)–O(21)–C(211)	126.6 (8)
O(31)–S–O(32)	113.0 (7)	P(1)–O(12)–C(121)	125.9 (8)	Fe–C(2)–O(2)	177.0 (12)	P(2)–O(22)–C(221)	122.5 (8)
Fe–C(1)–O(1)	178.3 (12)	P(1)–O(13)–C(131)	125.7 (8)	Fe–P(2)–O(21)	114.2 (4)	P(2)–O(23)–C(231)	125.4 (8)
Fe–P(1)–O(11)	114.2 (4)						

	x					
	11	12	13	21	22	23
O(x)–C(x1)–C(x2)	116 (1)	120 (1)	119 (1)	120 (1)	121 (1)	123 (1)
O(x)–C(x1)–C(x6)	122 (1)	118 (1)	121 (1)	118 (1)	114 (1)	117 (1)
C(x6)–C(x1)–C(x2)	122 (1)	122 (1)	120 (1)	121 (1)	125 (1)	119 (1)
C(x1)–C(x2)–C(x3)	119 (2)	117 (1)	120 (1)	120 (2)	117 (1)	121 (1)
C(x2)–C(x3)–C(x4)	121 (2)	121 (2)	121 (2)	120 (2)	124 (2)	120 (1)
C(x3)–C(x4)–C(x5)	118 (2)	122 (2)	120 (2)	120 (2)	116 (2)	120 (1)
C(x4)–C(x5)–C(x6)	120 (2)	118 (2)	121 (1)	120 (2)	121 (2)	120 (1)
C(x5)–C(x6)–C(x1)	118 (1)	120 (2)	118 (1)	118 (1)	117 (2)	120 (1)

Both molecules have C_2 symmetry (that of II is space group imposed) and almost exact trigonal-bipyramidal ligand distributions about the Fe atoms with interligand bond angles deviating by only a few degrees from ideal values (Table V and VI). However, whereas the phosphite ligands occupy axial coordination positions with CO groups equatorial in I (isomer A), they are equatorial with axial CO groups in II (isomer B). In both the SO$_2$ ligand is coordinated so that the FeSO$_2$ moieties are planar. However, in II this plane is almost exactly perpendicular to the equatorial plane of the complex (dihedral angle 89.5°), but it is not so in I, where the dihedral angle is 108.1°.

An important feature of the structure of I is the close approach of the O atoms of the SO$_2$ ligands to the estimated positions of the ortho-H atoms of the axial (PhO)$_3$P groups (especially C(132)H···O(32) = 2.57 Å, C(236)H···O(31) = 2.59 Å, C(212)H···O(31) = 2.86 Å, and C(112)H···O(32) = 2.95 Å). Some intramolecular contacts within the (PhO)$_3$P ligands are also rather short (C(216)H···O(22) = 2.61 Å, C(136)H···O(12) = 2.61 Å, C(122)H···O(11) = 2.69 Å, C-(222)H···O(21) = 2.69 Å, C(232)H···O(22) = 2.75 Å, and C(116)H···O(12) = 2.75 Å). In II the SO$_2$ ligand is sandwiched between two aromatic rings, one from each of the two equatorial phosphite ligands. The planes of these rings and that of the coordinated SO$_2$ molecule are almost parallel and rather close (separation ~3.4 Å). This suggests that there may be some degree of bonding between the three. However, if there is, it has no effects on the bond lengths and angles within the SO$_2$ ligand (cf. II and I, Tables VI–VII).

Comparable bond lengths and most bond angles within I and II are not significantly different (Table VII). The sole exceptions are the angles between non-SO$_2$ ligands, which lie

in the equatorial planes of the complexes. They are greater in II ($\angle$P–Fe–P = 123.3 (1)°) than in I ($\angle$C–Fe–C = 116.9 (7)°), clearly a consequence of steric effects.

The Fe–P distances in I and II (2.172 (5) and 2.167 (4) Å, respectively) are shorter than those found in [Fe(PPh$_3$)$_2$-(CO)$_2$(NNPh)]BF$_4$ (2.261 (2) and 2.266 (2) Å)[19] and [Fe-(PPh$_3$)(PMe$_3$)(CO)$_2$(η^2-CS$_2$)] (Fe–PPh$_3$ = 2.279 (1) and Fe–PMe$_3$ = 2.252 (2) Å)[20] and the Fe–phosphine distance in [Fe(CO)$_3$(P(OCH$_2$)$_3$P)Fe(CO)$_3$] (2.190 (4) Å) but are longer than the Fe–phosphite distance in the last complex (2.116 (4) Å).[21] Similar variations have been observed in Cr–P bond lengths in [Cr(L)(CO)$_5$] complexes (2.309 (1) Å when L = (PhO)$_3$P and 2.422 (1) Å when L = Ph$_3$P) and have been attributed, at least in part, to differences in Cr–L π backbonding.[22]

As compared with those in free SO$_2$, the S–O bond lengths are longer and the $\angle$O–S–O bond angles are smaller in both I and II.[5,6] The actual values are comparable with those found in other complexes containing planar η^1(S)-SO$_2$ ligands.[5,6] These changes in ligand dimensions are a consequence of the strong π-acceptor ability of η^1-planar SO$_2$ (see below).

IR Spectra. These are consistent with the presence of one or other of the [Fe(L)$_2$(CO)$_2$(SO$_2$)] isomers in the solid state but often with both in solution (see later). Apart from absorption bands due to L, which are not reported, there are those due to ν(CO) and ν(SO$_2$) vibrations, which are usually iden-

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Table VI. Bond Lengths and Angles, with Estimated Standard Deviations Given in Parentheses, for [Fe(P(OC$_6$H$_4$Me-o)$_3$)$_2$(CO)$_2$(SO$_2$)] (II)^a

(a) Distances (Å)

	Fe-P		2.167 (4)
Fe-S	2.055 (7)	S-O(S)	1.431 (14)
Fe-C(T)	1.811 (18)	C(T)-O(T)	1.122 (17)

	x		
	1	2	3
P-O(x)	1.60 (1)	1.60 (1)	1.59 (1)
O(x)-C(x1)	1.42 (2)	1.41 (2)	1.33 (2)
C(x1)-C(x2)	1.39 (2)	1.37 (2)	1.40 (2)
C(x2)-C(x3)	1.36 (3)	1.42 (2)	1.34 (3)
C(x3)-C(x4)	1.35 (3)	1.35 (3)	1.42 (4)
C(x4)-C(x5)	1.34 (3)	1.38 (3)	1.40 (4)
C(x5)-C(x6)	1.40 (2)	1.41 (3)	1.34 (3)
C(x6)-C(x1)	1.37 (2)	1.40 (2)	1.34 (2)
C(x6)-C(x7)	1.51 (2)	1.43 (2)	1.54 (3)

(a) Angles (deg)

C(T)-Fe-C(T')	178.0 (8)	C(T)-Fe-S	91.0 (5)
S-Fe-P	118.4 (1)	C(T)-Fe-P	89.8 (6)
P-Fe-P'	123.3 (1)	C(T)-Fe-P'	89.2 (6)
Fe-S-O(S)	123.1 (7)	Fe-P-O(3)	122.9 (5)
O(S)-S-O(S')	113.7 (11)	O(1)-P-O(2)	102.6 (6)
Fe-C(T)-O(T)	176.9 (16)	O(1)-P-O(3)	89.5 (6)
Fe-P-O(1)	118.8 (4)	O(2)-P-O(3)	106.6 (6)
Fe-P-O(2)	112.8 (4)		

	x		
	1	2	3
P-O(x)-C(x1)	125 (1)	130 (1)	133 (1)
O(x)-C(x1)-C(x2)	117 (1)	123 (1)	117 (2)
O(x)-C(x1)-C(x6)	121 (1)	113 (2)	125 (2)
C(x6)-C(x1)-C(x2)	122 (2)	123 (2)	117 (2)
C(x1)-C(x2)-C(x3)	120 (2)	121 (2)	124 (2)
C(x2)-C(x3)-C(x4)	118 (2)	116 (2)	113 (2)
C(x3)-C(x4)-C(x5)	123 (2)	122 (2)	124 (2)
C(x4)-C(x5)-C(x6)	120 (2)	124 (2)	114 (2)
C(x5)-C(x6)-C(x1)	116 (2)	113 (2)	125 (3)
C(x5)-C(x6)-C(x7)	124 (2)	122 (2)	116 (2)
C(x1)-C(x6)-C(x7)	119 (2)	125 (2)	119 (2)

^{a} Atoms marked with a prime are related to those at x, y, z by $-x$, y, $^1/_2 - z$.

Table VII. Comparison of Structural Data for [Fe(SO$_2$)(CO)$_2$(P(OR)$_3$)$_2$] Compounds (Distances in Angstroms and Angles in Degrees), with Estimated Standard Deviations Given in Parentheses

	R = phenyl	R = o-tolyl
	Distances	
Fe-S	2.051 (4)	2.055 (7)
S-O	1.45 (1)	1.43 (1)
O$_S$···O$_S$	2.42 (2)	2.40 (2)
Fe-P	2.172 (5)	2.167 (4)
Fe-C$_T$	1.78 (2)	1.81 (2)
C$_T$-O$_T$	1.14 (2)	1.12 (2)
P-O	1.60 (1)	1.60 (1)
	Angles	
Fe-S-O	123.5 (5)	123.1 (7)
O-S-O	113.0 (7)	113.7 (11)
S-Fe-X$_{eq}$^{a}	121.5 (5)	118.4 (1)
X$_{eq}$-Fe-X$_{eq}$	116.9 (7)	123.3 (1)
	Dihedral Angle	
SO$_2$/FeS(X$_{eq}$)$_2$	108.1	89.5

^{a} X$_{eq}$ refers to the other two atoms in the equatorial plane of the trigonal bipyramid about the Fe atom.

tified easily (Tables I and II).

Isomers A each give rise to two absorption bands in the 1900–2100-cm^{-1} region assignable to their ν(CO) modes. Those at higher frequencies are due to the symmetric and the

others to the asymmetric vibrations of the Fe(CO)$_2$ moieties. Their relative intensities are consistent with OC–Fe–CO angles of between 115 and 120°.[23] Isomers B give rise to single absorption bands between 1900 and 2100 cm^{-1}, which are assignable to the single IR-active, asymmetric ν(CO) modes of their *trans*-Fe(CO)$_2$ groups. The variations of the frequencies of these absorption bands with L are entirely conventional[24] and are consistent with all of these isomers having structures similar to those of [Fe(P(OPh)$_3$)$_2$(CO)$_2$(SO$_2$)] (I, isomer A) or [Fe(P(OC$_6$H$_4$Me-o)$_3$)$_2$(CO)$_2$(SO$_2$)] (II, isomer B).

The frequencies of the ν(CO) vibrations of both isomers suggest that the planar η^1(S)-SO$_2$ ligand is a very effective π-acceptor ligand. It appears to be slightly inferior to η^2-CS$_2$ and superior to CO. (In CS$_2$ solution for [Fe(PPh$_3$)$_2$(CO)$_3$] ν(CO) = 1886 and ca. 1959 cm^{-1},[25] and for [Fe(PPh$_3$)$_2$(CO)$_2$(η^2-CS$_2$)] ν(CO) = 1930 and 1993 cm^{-1}.[2]) However, as one goes from isomer A to B there is a marked increase in the frequency ($\sim$40 cm^{-1}) of the asymmetric ν(CO) mode of the Fe(CO)$_2$ moiety. This suggests that there is much less metal-to-CO back-bonding in B than in A, which may be a consequence of their trans disposition in the former.

The frequencies of the ν(CO) modes of both A and B increase along the solvent series CS$_2$, CHCl$_3$, and m-cresol. In most metal carbonyl complexes the reverse is true,[26] but it does happen in certain instances. For example, the μ-CO ligands of [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_4$] are relatively basic at oxygen and hydrogen bond strongly to protic solvents such as m-cresol. This results in an increase of their π-acceptor capacity and increases in the frequencies of the ν(CO) vibrations of the non-hydrogen-bonded CO ligands.[27] It is possible that a similar explanation may be applicable in the present case. SO$_2$ is a very powerful π-acceptor ligand and on coordination accepts electrons into its SO$_2$ π^* 2b$_1$ orbital, which would be expected to leave the O atoms more negatively charged and more basic. Interactions between those O atoms and the solvent which may extend to specific O···H bonding would increase the π-acceptor capability of SO$_2$ still further and bring about the observed increase in the frequencies of the ν(CO) vibrations in polar solvents.

In virtually all of the solid-state IR spectra strong absorption bands have been identified unambiguously in the 1070–1160- and 1230–1260-cm^{-1} regions, which have been assigned respectively to the asymmetric and symmetric ν(SO$_2$) modes of the SO$_2$ ligands (Table I). Their frequencies often lie outside the ranges (1085–1125 and 1245–1275 cm^{-1}) that have been suggested to be characteristic of planar η^1-SO$_2$ ligands in d^8 complexes. However, all are within or are extremely close to the proposed ranges for such ligands in d^6 (1065–1140 and 1225–1300 cm^{-1}) or d^{10} (1045–1120 and 1190–1290 cm^{-1}) systems and are well outside the ranges for pyramidal η^1-SO$_2$ in d^8 systems (990–1065 and 1150–1225 cm^{-1}).[6] There appears to be no systematic variation of ν(SO$_2$) frequency with either L or isomer type.

Isomerism. All of the complexes which we have prepared and listed in Table I are found as isomer A in the solid state except when L = (o-ClC$_6$H$_4$O)$_3$P, (o-MeC$_6$H$_4$O)$_3$P, and Ph-(o-MeC$_6$H$_4$O)$_2$P. These exist as isomer B. Solid-state effects appear to be responsible for the added complexity of the IR spectra between 1900 and 2100 cm^{-1} when L = (p-

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$ClC_6H_4O)_3P$, $(m\text{-MeC}_6H_4O)_3P$, $(p\text{-MeC}_6H_4O)_3P$, Ph-$(MeO)_2P$, $Ph_2(MeO)P$, and Ph_2MeP.

In solution many of the complexes exist as mixtures of A and B. The isomer ratio depends on both L and the solvent. Generally the importance of B increases and that of A declines along the solvent series cyclohexane $<$ CS$_2$ $<$ CHCl$_3$ $<$ MeCN $<$ *m*-cresol. This implies that B is the more polar of the two isomers in most instances.

The consequences of varying L are not straightforward. They appear to be dominated by steric factors, but electronic effects may also be important. The $(i\text{-PrO})_3P$ complex, which is a special case, will be discussed below. Otherwise in a given solvent the importance of A decreases and that of B increases along the series L = $Ph_3P \approx Ph_2MeP \approx Ph_2(MeO)P \approx Ph_2$-$(PhO)P \approx Ph(MeO)_2P \approx Ph(i\text{-PrO})_2P \approx (p\text{-ClC}_6H_4O)_3P <$ $Ph_2(o\text{-MeC}_6H_4O)P < Ph(PhO)_2P < (p\text{-MeC}_6H_4O)_3P <$ $(PhO)_3P < (m\text{-MeC}_6H_4O)_3P < Ph(o\text{-MeC}_6H_4O)_2P < (o\text{-}$ $MeC_6H_4O)_3P < (o\text{-ClC}_6H_4O)_3P$. The first seven compounds in this series exist solely as isomer A and the last solely as isomer B. It can be seen that generally B is favored by aryloxy groups attached to the ligating P atom and is disfavored by alkoxy, alkyl, and phenyl groups. The presence of ortho substituents on the PhO groups further tends to favor isomer B with the Cl group being more effective in this respect than Me. A *m*-Me substituent has an effect similar to but less marked than that of an *o*-Me group. On the other hand, para substituents would be expected to have no steric consequences of note. Therefore, the effects of replacing L = $(PhO)_3P$ by $(p\text{-XC}_6H_4O)_3P$ must be largely electronic in origin. These are negligible when X = Me, but when X is the strongly electron-withdrawing Cl, they cause A to be favored to the exclusion of B.

It is quite clear that increasing the bulk of triaryl phosphite ligands favors isomer B. However, this is not straightforward as Ph_3P and $(i\text{-PrO})_3P$ form complexes which adopt the A conformation exclusively both in the solid state and in solution even though the first has a larger cone angle than e.g. $(PhO)_3P$ and the second is comparable to it.[28] A possible explanation is that in both isomers the plane of the SO$_2$ ligand is ca. perpendicular to the equatorial coordination plane about Fe, but in A its O atoms interact strongly with the ortho protons of the two axial $(PhO)_3P$ ligands with estimated *o*-H···OS separations as low as 2.57 Å (C(ortho)···OS = 3.25 (2) Å). Presumably the ligands adopt orientations about the Fe–P and P–O bonds that reduce these steric interactions and those within the $(PhO)_3P$ groups to a minimum. However, they still prevent the SO$_2$ ligand from lying exactly perpendicular to the Fe(CO)$_2$S plane. If *o*-Me groups replace the *o*-H, SO···M(phosphite) nonbonded interactions must become large either because of direct *o*-Me···OS contacts or because the *o*-Me groups prevent the triaryl phosphite ligands from adopting conformations that would reduce *o*-H···OS interactions to an acceptable value. Therefore the molecule A is destabilized with respect to B, which has the two phosphite ligands equatorial. As a consequence of the A → B isomerization, the steric interactions between the SO$_2$ group and the axial ligands are so reduced that they are probably negligible, and the SO$_2$ plane in B lies perpendicular to the equatorial plane of the complex. The consequence of having two close triaryl phosphite ligands in B (P–Fe–P angle = 123.3 (1)°) clearly are not energetically unacceptable. However, the unwillingness of certain complexes to form isomer B may be due to the destabilization of B by L–L interactions when L is a phosphine with a relatively large cone angle[28] and the stabilization of A because of reduced intra- and interligand interactions when L is not bulky.

The IR spectrum of $[Fe(P(OPr\text{-}i)_3)_2(CO)_2(SO_2)]$ in the 1900–2100-cm^{-1} region is more complicated than those of other complexes both in the solid state and in solution. However, isomer B is not present, and it is possible that, in this isomer A, rotation about the Fe–P and P–O bonds is partially restricted so that two rotational isomers are present. One would give rise to the ν(CO) absorption bands at 1945 and 2003 cm^{-1} and the other to those at 1934 and 1995 cm^{-1} (Table I).

The interconversion of isomers A and B is clearly a facile process. This is not surprising because it requires a single Berry pseudorotation. In the square-pyramidal intermediate for this process, the SO$_2$ ligand occupies the apical coordination position and rotates through 90° during the isomerization. Square-pyramidal d^8 metal–SO$_2$ complexes are common.[5,6] All have an apically coordinated pyramidal η^1(S)-SO$_2$ ligand in which there is no longer any symmetry distinction between σ and π orbitals on both ligand and metal. Consequently rotation about the Fe–S bond is probably a low-energy process (whereas it is not in A and B) even though certain conformations are to be preferred.[5,6] On the other hand, the formation of an apical R$_3$P–axial CO isomer of $[Fe(PR_3)_2\text{-}(CO)_2(SO_2)]$ would require at least two Berry pseudorotations via square-pyramidal intermediates with nonapical SO$_2$ ligands, and SO$_2$ appears to be a strongly apicophilic ligand.

Bonding. The bonding between the planar η^1-SO$_2$ ligand and the trigonal-bipyramidal $Fe(PR_3)_2(CO)_2$ fragment of C_{2v} symmetry has been described in ref 5 and 6. Briefly, it involves S to Fe donation of electrons from the filled SO$_2$ 4a$_1$ orbital into the vacant metal 2a$_1$ LUMO with back-donation from the filled metal b$_2$ HOMO, which lies in the equatorial (xz) plane of the complex, into the vacant SO$_2$ 2b$_1$ orbital, which lies perpendicular to the SO$_2$ plane. Although the S to Fe σ-bonding is axially symmetric, the Fe to S back-bonding is not and as a consequence the plane of the SO$_2$ ligand is perpendicular to the equatorial plane of the complex. The importance of the b$_2$ → 2b$_1$ back-bonding is so great that the L$_{axial}$–SO$_2$ interactions in A do not force the SO$_2$ ligand to rotate through 90° and interact with the filled b$_1$ metal orbital of much lower energy, which would be a poorer π-donor. Instead, axial and equatorial ligands interchange to give isomer B with its increased L–L interactions. However, there is a further and positive aspect to such an isomerization. As outlined in ref 6 and 29, the interaction of the lone pairs of the two equatorial CO ligands in A with the metal 3d$_{xz}$ and 4p$_x$ orbitals increases the energy of the metal b$_2$ HOMO. Replacement of CO by the stronger σ-donor ligands L may increase this still further and render the Fe → SO$_2$ back-bonding even more important. It may be this last aspect that causes the $(p\text{-ClC}_6H_4O)_3P$ complex not to adopt the B structure as the electronic effect of the electron-withdrawing *p*-Cl would be expected to make it a poorer σ-donor than e.g. $(PhO)_3P$.

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$(CO)_2(SO_2)]$ (isomer A), 87336-15-0; $[Fe(Ph_2(o\text{-}MeC_6H_4O)P)_2\text{-}(CO)_2(SO_2)]$, 87392-57-2; $[Fe(Ph_2(MeO)P)_2(CO)_2(SO_2)]$, 87336-16-1; $[Fe(Ph_2MeP)_2(CO)_2(SO_2)]$, 87336-17-2; $[Fe(Ph_3P)_2(CO)_2(SO_2)]$, 87336-18-3; $[Fe(P(OC_6H_4Cl\text{-}p)_3)_2(CO)_3]$, 87319-47-9; $[Fe(P(OC_6H_4Cl\text{-}o)_3)_2(CO)_3]$, 87319-48-0; $[Fe(Ph_3P)_2(CO)_2(\eta^2\text{-}CS_2)]$, 86196-40-9; $[Fe((i\text{-}PrO)_3P)_2(CO)_2(\eta^2\text{-}CS_2)]$, 87336-20-7; $[Fe((PhO)_3P)_2(CO)_2(\eta^2\text{-}CS_2)]$, 66808-76-2; $[Fe((o\text{-}MeC_6H_4O)_3P)_2\text{-}(CO)_2(\eta^2\text{-}CS_2)]$, 72573-16-1; $[Fe((m\text{-}MeC_6H_4O)_3P)_2(CO)_2(\eta^2\text{-}CS_2)]$, 87336-21-8; $[Fe((p\text{-}MeC_6H_4O)_3P)_2(CO)_2(\eta^2\text{-}CS_2)]$, 72557-45-0; $[Fe(Ph(PhO)_2P)_2(CO)_2(\eta^2\text{-}CS_2)]$, 87336-22-9; $[Fe(Ph(o\text{-}MeC_6H_4O)_2P)_2(CO)_2(\eta^2\text{-}CS_2)]$, 87336-23-0; $[Fe(Ph(MeO)_2P)_2\text{-}(CO)_2(\eta^2\text{-}CS_2)]$, 87336-24-1; $[Fe(Ph(i\text{-}PrO)_2)P)_2(CO)_2(\eta^2\text{-}CS_2)]$, 87336-25-2; $[Fe(Ph_2(PhO)P)_2(CO)_2(\eta^2\text{-}CS_2)]$, 87336-26-3; $[Fe(Ph_2(o\text{-}MeC_6H_4O)P)_2(CO)_2(\eta^2\text{-}CS_2)]$, 87336-27-4; $[Fe(Ph_2(MeO)P)_2(CO)_2(\eta^2\text{-}CS_2)]$, 87336-28-5; $[Fe(Ph_2MeP)_2(CO)_2(\eta^2\text{-}CS_2)]$, 72557-50-7.

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Preparation of Thia- and Selenacarborane Derivatives by Carbon Atom Insertion with Isocyanide Derivatives

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Alkyl isocyanides react at room temperature with $B_9H_{11}E$ (E = S or Se) to initially form two isomeric $B_9H_{11}E\cdot CNR$ compounds. One of these isocyanide-complexed intermediates reacted further to form the carborane derivative $B_9H_9ECNH_2R$ in good yield. The second $B_9H_{11}E\cdot CNR$ compound did not undergo further reaction even in refluxing toluene. Treatment of $B_9H_{11}S$ with sodium cyanide formed $Na[B_9H_{11}S\cdot CN]$. This cyano complex was converted to $B_9H_9SCNH_3$ by passing the salt through a column of acid ion-exchange resin.

Introduction

The reaction of $BH_3\cdot O(C_2H_5)_2$ and various alkyl-substituted derivatives with organic compounds containing carbon–carbon double or triple bonds (hydroboration) has been extensively studied.[1,2] Similar reactions of an ether solution of BH_3 with aldehydes, ketones, and azo compounds have been reported.[3] Diborane(6) and alkylboranes add across the carbon–nitrogen multiple bond of alkyl isocyanide derivatives as well.[4–6]

Reactions of higher boron hydrides with multiple-bonded functional groups have been studied for nearly 30 years, but on a relatively limited scale. Acetylenes, for example, react with higher boron hydrides to give three distinctly different types of products. The reaction $B_9H_{11}S$ with acetylene forms $B_9H_{10}(CH=CH_2)S$ in which the alkenyl groups is exo to the cage framework and is bonded to one of the boron atoms.[7] This is an example of a simple hydroboration. A second type of reaction involves the incorporation of both carbon atoms of the acetylene into the cage framework as illustrated by eq 1.[8,9] The mechanism for this reaction is not understood. The
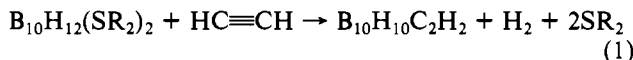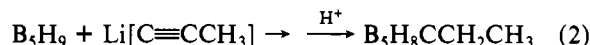
$$B_{10}H_{12}(SR_2)_2 + HC\equiv CH \rightarrow B_{10}H_{10}C_2H_2 + H_2 + 2SR_2 \quad (1)$$

third type of reaction involves incorporation of only one of the acetylene carbon atoms into the cage structure as exemplified by eq 2.[10] This reaction can be viewed as an intramolecular

$$B_5H_9 + Li[C\equiv CCH_3] \rightarrow \xrightarrow{H^+} B_5H_8CCH_2CH_3 \quad (2)$$

bishydroboration of the acetylide ion.

Alkyl isocyanides, which are isoelectronic with the acetylide ion, also undergo a bishydroboration type reaction with decarborane (14) (eq 3).[11] Subsequently $i\text{-}B_{18}H_{22}$[12] and Na-

$$B_{10}H_{14} + C\equiv NCH_3 \rightarrow B_{10}H_{12}CNH_2CH_3 \quad (3)$$
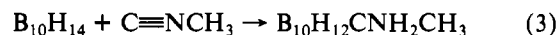
$[B_{10}H_{13}]$[13] were found to react with alkyl and aryl isocyanides, respectively, to form similar one-carbon carborane derivatives.

It is quite possible that isocyanide derivatives as well as other polar multiple-bonded reagents will undergo multiple hydroboration reactions with a variety of nido and arachno higher boron hydride derivatives. In this paper we describe our initial studies concerning the reactions of isocyanide derivatives with

Table I. Elemental Analyses of the Thia- and Selenacarborane Derivatives

compd	% calcd		% found	
	C	H	C	H
$B_9H_9SCNH_2(t\text{-}C_4H_9)$ (I)	26.87	9.01	26.23	8.85
$B_9H_9SCNH_2(C_6H_{11})$ (II)	33.68	8.84	33.71	8.88
$B_9H_9SCN(CH_3)_2(t\text{-}C_4H_9)$ (III)	33.42	9.61	33.35	9.54
$B_9H_9SeCNH_2(C_6H_{11})$ (V)	28.36	7.48	28.31	7.67

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