of electrochemical equipment.

Registry No. $W_2Cl_4(PBu_3)_4$, 73133-23-0; $W_2Cl_4(PMe_3)_4$, 73495-54-2; $W_2Cl_4(PMe_2Ph)_4$, 73133-21-8; $W_2Cl_4(PMePh_2)_4$, 73133-22-9; $W_2Cl_4(dmpe)_2$, 73133-09-2; $W_2Cl_4(dppe)_2$, brown isomer, 73133-24-1; $W_2Cl_4(dppe)_2$, green isomer, 86782-93-6; $W_2Cl_6(THF)_4$, 77479-88-0; $W_2Cl_6(PMe_3)_4$, 73146-59-5; $W_3O_3Cl_5(CH_3CO_2)(PBu_3)_3$, 73470-14-1; $[W_2Cl_4(PBu_3)_4]^+PF_6^-$, 86728-81-6; $[W_2Cl_6(PMe_3)_4]^+[CF_3SO_3]^-$, 86747-51-5; $Na_4(DME)_4W_2Cl_8$, 86747-52-6; $Na_4(TMEDA)_4W_2Cl_8$, 83232-09-1; $W_2(mhp)_4$, 67634-84-8; $W_2(O_2CCMe_3)_4$, 86728-84-9; $Mo_2Cl_4(PBu_3)_4$, 39306-31-5; WCl_4, 13470-13-8; $FeCp_2^+OTf^-$, 86728-83-8; $[Ag(MeCN)_4]^+PF_6^-$, 86728-82-7; W, 7440-33-7.

Contribution from the School of Chemical Sciences,
University of Illinois, Urbana, Illinois 61801

Synthesis and Reactivity of $[Ir(\eta^2\text{-}E_2R)(Ph_2PCH_2CH_2PPh_2)_2]^{2+}$ (E = S, Se; R = H, CH_3)

JOHN E. HOOTS and THOMAS B. RAUCHFUSS*

Received October 19, 1982

The stereochemistry and reactivity of $[Ir(E_2R)(dppe)_2]^{2+}$ (dppe = $Ph_2P(CH_2)_2PPh_2$; E = S, Se; R = H, CH_3) have been examined. In solution, $[Ir(E_2CH_3)(dppe)_2]^{2+}$ exists as a mixture of two diastereomers in the ratio of 20:1 (E = S) and 6:1 (E = Se). Protonation of $[Ir(E_2)(dppe)_2]^+$ with strong acids gave $[Ir(E_2H)(dppe)_2]^{2+}$ complexes, which are spectroscopically and stereochemically similar to the η^2-E_2CH_3 derivatives. In contrast to $[Ir(S_2)(dppe)_2]^+$, the $[Ir(S_2CH_3)(dppe)_2]^{2+}$ (**1**) complex can act as both a potent sulfur atom and CH_3S^+ transfer reagent. The nature of the S-transfer reaction depends on the substrate (X) used and the stability of the corresponding S–X and $[X\text{–}SCH_3]^+$ products. **1** reacts rapidly with PPh_3 (2 equiv) to give $[Ir(dppe)_2]^+$, Ph_3PS, and $[Ph_3PSCH_3]^+$. With CH_3NC (2 equiv) and **1**, sulfur atom transfer occurs, and *cis*-$[Ir(SCH_3)(CH_3NC)(dppe)_2]^{2+}$ and CH_3NCS are produced. Reaction of CN^- with **1** gave *cis*-$[Ir(SCH_3)(SCN)(dppe)_2]^+$. Oxidative addition of CH_3SH and CH_3SCl to $[Ir(dppe)_2]^+$ gave $[Ir(SCH_3)H(dppe)_2]^+$ and $[Ir(SCH_3)Cl(dppe)_2]^+$, respectively. ^1H NMR species confirmed the utility of the high-field ortho phenyl, the S_2CH_3, and the SCH_3 resonances in structure elucidation. Also described is the applicability of gel-permeation chromatography and field-desorption mass spectrometry for the purification and characterization of these ionic, high molecular weight complexes.

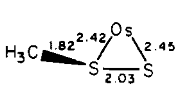
Introduction

In recent years, considerable attention has been directed toward the synthetic and catalytic chemistry of metal sulfides. Within the realm of sulfur-rich metal complexes, the reactivities of disulfur and pentasulfido ligands have been particularly fruitful areas of research.[1,2] A second class of sulfur-rich metal complexes, the perthiocarboxylates, has also received considerable attention.[3]

In this report, we describe reactivity studies on the simplest organic perthio ligand, S_2CH_3, as found in $[Ir(\eta^2\text{-}S_2CH_3)(dppe)_2]^{2+}$ (dppe = $Ph_2PCH_2CH_2PPh_2$). Salts of this ion were first prepared in 1979 via the alkylation of $[Ir(S_2)(dppe)_2]^+$:[4]

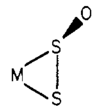
$$[Ir(S_2)(dppe)_2]^+ \xrightarrow[25\,°C]{CH_3OSO_2F} [Ir(\eta^2\text{-}S_2CH_3)(dppe)_2]^{2+} \quad (1)$$

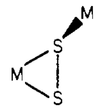
The geometry about the perthio ligand in this iridium complex is presumed to resemble that found crystallographically in $[Os(\eta^2\text{-}S_2CH_3)(CO)_2(PPh_3)_2]ClO_4$:[5]



∠SOsS = 49.1°
∠OsSS = 65.9°, 65.0°
∠SSC = 105.4°
∠OsSC = 117.4°

As such, the η^2-S_2CH_3 ligand is structurally and electronically related to other derivatives of the S_2 ligand such as





which can be found, inter alia, in $[Ir(S_2O)(dppe)_2]Cl$[6] and $[Mo_4(NO)_4S_{13}]^{4-}$,[7] respectively. Therefore, characterization of the reactivity of the η^2-S_2CH_3 ligand is relevant to the chemistry of other sulfur-rich metal complexes.

Cysteine perthiolate ligation has been considered in the context of two enzymatic processes. Arguments have been advanced that both rhodanese[8] and xanthine oxidase[9] contain perthiolates at their active sites. Characteristic reactions of each enzyme involve the formation of thiocyanate upon treatment with cyanide (eq 2). In the case of xanthine oxidase, this process deactivates the enzyme,[10] while eq 2 is but one of the many manifestations of the catalytic sulfur-transfer properties of rhodanese.[8]

$$E\cdot S + CN^- \rightarrow E + SCN^- \quad (2)$$

Reactivity studies on η^2-S_2CH_3 complexes bear on the chemistry of the η^2-O_2R ligand, which is presumed to be a

---

(1) Müller, A.; Jaegermann, W.; Enemark, J. H. *Coord. Chem. Rev.* **1982**, *46*, 245. Bolinger, C. M.; Rauchfuss, T. B.; Rheingold, A. L. *Organometallics* **1982**, *1*, 1551 and references therein.

(2) Bolinger, C. M.; Rauchfuss, T. B. *Inorg. Chem.* **1982**, *21*, 3947 and references therein.

(3) Fackler, J. P., Jr.; Fetchin, J. A.; Fries, D. C. *J. Am. Chem. Soc.* **1973**, *94*, 7323 and references therein.

(4) Plute, K. L. K.; Haltiwanger, R. C.; Rakowski DuBois, M. *Inorg. Chem.* **1979**, *18*, 3246.

(5) Clark, G. R.; Russell, D. R. *J. Organomet. Chem.* **1979**, *173*, 377.

(6) Schmid, G.; Ritter, G. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 645.

(7) Müller, A.; Eltzner, W.; Mohan, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 168.

(8) Sörbo, B. In "Metabolic Pathways"; Greenberg, D. M., Ed.; Academic Press: New York, 1975; pp 433–453. Westley, J. *Adv. Enzymol. Relat. Areas Mol. Biol.* **1973**, *39*, 327.

(9) Massey, V.; Edmondson, D. *J. Biol. Chem.* **1970**, *245*, 6595. Coughlan, M. P. "Molybdenum and Molybdenum-Containing Enzymes"; Pergamon Press: New York, 1980; pp 148–149. Stiefel, E. I. *Ibid.*, pp 73–74, 88–90.

(10) Gutteridge, S.; Tanner, S. J.; Bray, R. C. *Biochem. J.* **1978**, *175*, 887.

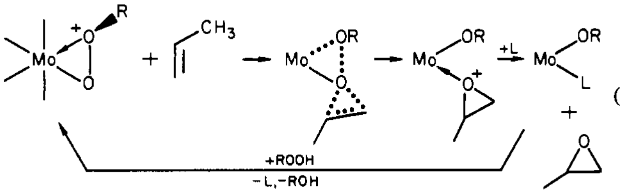
0020-1669/83/1322-2806$01.50/0

Table I. Analytical Data[a]

compd	% C	% H	% P	% N	% S	% Cl
$[Ir(Se_2CH_3)(dppe)_2](PF_6)_2$	43.65 (43.84)	3.54 (3.54)	12.77 (12.80)			
cis-$[Ir(SCH_3)(CH_3NC)(dppe)_2](PF_6)_2\cdot H_2O$	47.52 (47.69)	3.72 (4.08)		1.19 (1.01)	2.01 (2.31)	
cis-$[Ir(SCH_3)(SCN)(dppe)_2]PF_6$	52.16 (52.34)	4.26 (4.15)		1.03 (1.13)	4.62 (5.17)	
trans-$[Ir(SCH_3)H(dppe)_2]PF_6$	53.45 (53.85)	4.82 (4.43)			2.57 (2.71)	0.0
trans-$[Ir(SCH_3)Cl(dppe)_2]PF_6$	52.12 (52.37)	4.12 (4.15)	12.72 (12.74)		2.55 (2.64)	2.91 (2.92)
cis-$[IrCl_2(dppe)_2(dppe)_2PF_6\cdot{}^1/_4CH_2Cl_2$	51.54 (51.18)	3.78 (3.99)	12.74 (12.63)		0.0	7.00 (7.23)

[a] Calculated values are in parentheses.

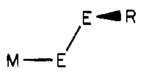
central feature of certain metal-catalyzed oxygen atom transfer reactions. For instance, molybdenum derivatives of the η^2-O_2R moiety have been invoked as intermediates in the Oxirane process (R = *tert*-butyl) for the catalytic production of propylene oxide (eq 3).[11,12] An analogous mechanism has been

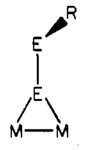


(3)

proposed by Sharpless for the $VO(OR)_3$-catalyzed epoxidation of allylic alcohols with *tert*-butyl hydroperoxide.[13] With adoption of the η^2-ligation mode, the electrophilicity of the peroxide oxygen atom is enhanced, thereby facilitating attack on the carbon–carbon double bond. The lability of such peroxide complexes together with the fragile character of the O–O bond militates against isolation of stable complexes containing η^2-O_2R ligands. To our knowledge, stable and characterized compounds of this type have not been reported previously in the literature. In the present case, the considerable strength of the S–S bond and the exchange-inert character of octahedral iridium(III) complexes stabilize the analogous η^2-S_2CH_3 ligand and permit characterization of its sulfur atom transfer reactivity. The utility of using sulfur analogues of oxygenates in mechanistic organometallic studies is particularly well illustrated in recent work by Roper and co-workers.[14]

Although this report concentrates on the η^2-E_2R (E = S, Se) ligand, it is noteworthy that the E_2R system does exhibit a variety of coordination modes.





Examples of η^1-coordination are $IrCl_2(CO)(PPh_3)_2(SSC_6F_5)$,[15a] which is formed via oxidative addition of $C_6F_5S_2Cl$ to Vaska's complex, and $Os(Se_2CH_3)H(CO)_2(PPh_3)_2$,[15b] which is formed from the corresponding cationic η^2-Se_2CH_3 complex upon treatment with $NaBH_4$. A bridging S_2-*t*-Bu ligand was recently found for $Cp_2Cr_2(t\text{-}BuS_2)(t\text{-}BuS)(NO)_2$.[15c]

Experimental Section

All standard ^1H NMR spectra were obtained (at 360 MHz) on a Nicolet NT-360 spectrometer using internal references at 18 °C. $^{31}P\{^1H\}$ NMR spectra were obtained (at 40.5 MHz) on a modified Varian XL-100 spectrometer at 25 °C using an external D_2O lock with 85% H_3PO_4 as an external reference (downfield shifts are positive). IR spectra were obtained with KBr disks on a Perkin-Elmer 599B spectrophotometer. UV–vis spectra were recorded with a Varian Cary 219 spectrophotometer. Field-desorption and fast-atom-bombardment mass spectra[16] were run on a Varian 731 spectrometer by Carter Cook. Microanalyses were performed by the School of Chemical Sciences analytical laboratory and are collected in Table I.

Reactions were performed under nitrogen in reagent grade solvents. CH_2Cl_2 was distilled from P_2O_5 under nitrogen. Toluene and benzene were distilled under nitrogen from Na and Na–benzophenone, respectively. Workup of iridium(III) products was done in air and simply involved the use of solvents dried over 3-Å molecular sieves. Bio-Beads S-X 2 and S-X 4 gel-permeation resins were purchased from Bio-Rad Laboratories. CH_3SH, CF_3SO_3H, CH_3SO_3F, and all substituted phosphines were purchased commercially. The preparations of $IrCl(CO)(PPh_3)_2$,[17] $(C_5H_5)_2TiSe_5$,[2] CH_3NCS,[18] CH_3NCSe,[19] and CH_3SCl[20] are described in the literature. CH_3SCl can be stored for several weeks without decomposition at dry-ice or liquid-N_2 temperatures. $[Ir(S_2)(dppe)_2]Cl$ was prepared according to the literature[21] from $[Ir(dppe)_2]Cl$. An improved synthesis of $Ir(dppe)_2^+$ is described below.

$[IrCO(dppe)_2]X$. To a mixture of *trans*-$IrCl(CO)(PPh_3)_2$ (3.8 g, 4.9 mmol) and dppe (4.1 g, 10 mmol) was added CH_2Cl_2 (50 mL). The solution was stirred for 10 min and then evaporated to dryness. The residue was transferred to a Schlenk filter flask, and the solids were extracted with (1:1 v/v) toluene–hexanes (25-mL portions) until silica gel TLC indicated no residual PPh_3 or dppe. After drying, a 97% yield (5.0 g) of $[IrCO(dppe)_2]Cl$ was obtained as a light yellow powder. IR (Nujol): ν_{CO} = 1927 (vs) cm^{-1}. Metathesis to the PF_6^- salt was effected by the addition of a MeOH solution (35 mL) of NH_4PF_6 (2.0 g, 12 mmol) to a stirred solution of $[IrCO(dppe)_2]Cl$ (1.98 g, 1.88 mmol) in a slight excess of CH_2Cl_2. Additional CH_2Cl_2 was added until the solids dissolved, and then the slurry was evaporated to complete dryness. The residue was extracted with CH_2Cl_2 and filtered, and the extract was evaporated to dryness. This afforded a 95% yield (2.16 g) of $[IrCO(dppe)_2]PF_6\cdot{}^1/_2CH_2Cl_2$ as a light yellow powder. Throughout both procedures, all solids were stored under CO and all manipulations done in a N_2 atmosphere.

---

(11) Parshall, G. W. *J. Mol. Catal.* **1978**, *4*, 243.

(12) Parshall, G. W. "Homogeneous Catalysis"; Wiley-Interscience: New York, 1980; pp 115–117. Sheldon, R. A.; Kochi, J. K. "Metal-Catalyzed Oxidations of Organic Compounds"; Academic Press: New York, 1981; pp 56–62.

(13) Sharpless, K. B.; Verhoeven, T. R. *Aldrichimica Acta* **1979**, *12*, 63.

(14) Collins, T. J.; Roper, W. R. *J. Organomet. Chem.* **1978**, *159*, 73. Roper, W. R.; Town, K. G. *J. Chem. Soc., Chem. Commun.* **1977**, 781.

(15) (a) Bhattacharya, S. N.; Senoff, C. V.; Walker, F. S. *Inorg. Chim. Acta* **1980**, *44*, L273. (b) Farrar, D. H.; Grundy, K. R.; Payne, N. C.; Roper, W. R.; Walker, A. *J. Am. Chem. Soc.* **1979**, *101*, 6577. (c) Eremenko, I. L.; Pasynskii, A. A.; Kilinnikov, V. T.; Struchkov, Y. T.; Aleksandrov, G. G. *Inorg. Chim. Acta* **1981**, *52*, 107.

(16) Barber, M.; Bordoli, R. S.; Sedgwick, R. D.; Tyler, A. N. *J. Chem. Soc., Chem. Commun.* **1981**, 325.

(17) Collman, J. P.; Sears, C. T., Jr.; Kubota, M. *Inorg. Synth.* **1968**, *11*, 102.

(18) Moore, M. L.; Crossley, F. S. *Org. Synth.* **1941**, *21*, 81.

(19) Franklin, W. J.; Werner, R. L. *Tetrahedron Lett.* **1965**, 3003.

(20) Douglas, I. B. *J. Org. Chem.* **1959**, *24*, 2004.

(21) Ginsberg, A. P.; Lindsell, W. E.; Sprinkle, C. R.; West, K. W.; Cohen, R. L. *Inorg. Chem.* **1982**, *21*, 3666.

$[Ir(dppe)_2]X$. To $[IrCO(dppe)_2]Cl$ (2.38 g, 2.26 mmol) was added toluene (100 mL). The slurry was stirred and refluxed for 8 h, and the atmosphere in the reaction vessel was flushed with fresh N_2 every hour. Progress of the reaction was monitored by IR spectroscopy. The solvent was evaporated in vacuo with gentle warming. After the residue was dried, a 97% yield (2.26 g) of orange-red powder was obtained. ^1H NMR and IR spectroscopy showed the product to be free of $[IrH(dppe)_2]$[22] and $[IrCO(dppe)_2]^+$ impurities.[23] Similar results were obtained by starting with $[IrCO(dppe)_2]PF_6$ and by using benzene as a decarbonylation solvent.

$[Ir(Se_2)(dppe)_2]Cl{\cdot}2CH_2Cl_2$. To a mixture of $[Ir(dppe)_2]Cl$ (1.03 g, 1.01 mmol) and Cp_2TiSe_5 (0.58 g, 1.01 mmol) was added 60 mL of (2:1 v/v) THF–CH_2Cl_2. After being stirred for 3 h, the solution was evaporated to dryness. The residue was chromatographed on Bio-Beads S-X 4 and eluted with CH_2Cl_2. The green band, which eluted first, was concentrated and then diluted with Et_2O or THF. This afforded an 88% yield (1.20 g) of dark green microcrystals. Drying of the sample at 60 °C in vacuo results in the conversion to a $^1/_4CH_2Cl_2$ solvate. An investigation of the actual rate of reaction by 360-MHz ^1H NMR spectroscopy, at concentrations identical with those above, revealed that the reaction was complete within 10 min.[24]

$[Ir(\eta^2\text{-}S_2CH_3)(dppe)_2](PF_6)_2$ (1). This compound was synthesized according to the literature method.[4] Purification was effected by chromatography on Bio-Beads S-X 2 and eluted with CH_2Cl_2. The major (yellow) fraction, which eluted first, was recrystallized from acetone–methanol. A minor (orange) fraction, which eluted directly behind $[Ir(S_2CH_3)(dppe)_2]^{2+}$, was found by ^1H NMR spectroscopy to be unreacted $[Ir(S_2)(dppe)_2](PF_6)$.

$[Ir(\eta^2\text{-}Se_2CH_3)(dppe)_2](PF_6)_2$. To a CH_2Cl_2 solution (25 mL) of $[Ir(Se_2)(dppe)_2]Cl{\cdot}2CH_2Cl_2$ (0.114 g, 84 μmol) was added 30 μL (~0.36 mmol) of 97% CH_3OSO_2F. After the solution was stirred for 36 h, an additional 50 μL (~0.60 mmol) of the 97% CH_3OSO_2F was added. After a further 24 h, the solution was evaporated, and the crude product was metathesized to the PF_6^- salt by using the procedure described for $[IrCO(dppe)_2]PF_6$. The final product was obtained by dilution of a warm (1:1 v/v) CH_2Cl_2–CH_3OH solution with hexanes, followed by cooling to −25 °C. Yield: 75% (92 mg) of red-orange powder. ^1H NMR (360 MHz) spectroscopy was used to examine the fluxional behavior of this compound in CD_3NO_2 solution; the spectra were recorded at 20, 50, and 80 °C. After this experiment, a final 20 °C spectrum indicated that only minimal decomposition had occurred.

Protonation of $[Ir(E_2)(dppe)_2]^+$. For ^1H NMR studies, $[Ir(E_2)(dppe)_2]Cl$ (5 mg) was added to a 5-mm NMR tube, and the solids were dissolved in CD_2Cl_2. A small amount of 3-Å molecular sieves was added, and the solution was swirled periodically on a vortex mixer until ^1H NMR spectroscopy indicated the solution was anhydrous. An excess of neat CF_3SO_3H was slowly added by syringe. Distinctive color changes for the disulfur and diselenium complexes indicated complete protonation. For spectrophotometric studies, $[Ir(E_2)(dppe)_2]Cl$ (3–5 mg) was added to a Pyrex cuvette and the solids were dissolved with $CHCl_3$. An excess of CF_3SO_3H was added to effect protonation of the complexes. The protonation reaction can be reversed with MeOH or THF for the disulfur complex and *tert*-butylamine for the diselenium complex.

***cis*-$[Ir(SCH_3)(CH_3NC)(dppe)_2](PF_6)_2{\cdot}H_2O$.** To a stirred solution of $[Ir(S_2CH_3)(dppe)_2](PF_6)_2$ (0.13 g, 95 μmol) in CH_2Cl_2 (20 mL) was added dropwise a 10% w/v solution of CH_3NC in CH_2Cl_2 (94 μL, 0.23 mmol). The solution was stirred 2 h and refluxed 8 h, during which a pale precipitate formed. The suspension was evaporated to dryness, and the residue was washed with 5 mL of CH_2Cl_2. A second crop was obtained by washing the evaporated filtrate with a small aliquot of CH_2Cl_2. A combined yield of 43% (57 mg) of light yellow powder was obtained. IR (Nujol): ν_{CN} = 2245 (s) cm^{-1}.

***cis*-$[Ir(SCH_3)(SCN)(dppe)_2]PF_6$.** A MeOH solution (1 mL) of NaCN (2.4 mg, 49 μmol) was added dropwise to a stirred MeOH solution (15 mL) of $[Ir(S_2CH_3)(dppe)_2](PF_6)_2$ (61 mg, 44 μmol). A precipitate formed rapidly, and CH_2Cl_2 (10 mL) was added to obtain a homogeneous solution. After being stirred overnight, the solution was evaporated to dryness. The residue was extracted with CH_2Cl_2 and filtered, and the extract was evaporated to dryness. The solids were dissolved in $CHCl_3$, and the solution was concentrated in vacuo and cooled to −25 °C. Filtration, followed by washing with a minimum of $CHCl_3$ and drying, afforded 64% yield (35 mg) of light yellow microcrystals. IR (thin film): ν_{CN} = 2100 (m) cm^{-1}.

Reactions of $[Ir(S_2CH_3)(dppe)_2](PF_6)_2$ with $(CH_3)_2PhP$. In a 5-mm NMR tube, $[Ir(S_2CH_3)(dppe)_2](PF_6)_2$ (85 mg, 62 μmol) was dissolved in (1:1 v/v) $CDCl_3$–CD_2Cl_2. Two successive additions of $(CH_3)_2PhP$ (9.0 μL, 63 μmol each) were monitored by ^1H NMR spectroscopy. A color change from yellow to orange was complete within seconds. On the basis of the integrated NMR spectrum, $[(CH_3)_2PhPSCH_3]PF_6$,[25] $(CH_3)_2PhPS$,[25] and $[Ir(dppe)_2]PF_6$ all were formed cleanly in equal amounts.

The analogous reaction using PPh_3 was monitored by 360-MHz ^1H NMR spectroscopy and silica gel TLC; the results were very similar to those of the $(CH_3)_2PhP$ experiment.[26] In addition, visible spectrophotometry was used to ascertain the relative rate of the PPh_3 reaction in comparison to that of a previously reported reaction using $EtPh_2P$ and $[Ir(S_2)(dppe)_2]Cl$.[21] In a 1.00-cm path length Pyrex cuvette containing a micro-stirbar, $[Ir(S_2CH_3)(dppe)_2](PF_6)_2$ (5.0 mg, 3.7 μmol) was dissolved in MeCN (2.4 mL). To that stirred solution was quickly added a MeCN solution (0.3 mL) of Ph_3P (2.0 mg, 7.6 μmol). The disappearance of $[Ir(S_2CH_3)(dppe)_2]^{2+}$ was followed by monitoring the absorbance (at 416 nm) vs. time for 1 h, after which 4—5 molar equiv of additional Ph_3P was dissolved in the solution. The absorbance at 416 nm was monitored for another 40 min, and no change was observed.

***trans*-$[IrH(SCH_3)(dppe)_2]PF_6$.** Gaseous MeSH was bubbled through a stirred CH_2Cl_2 solution (15 mL) of $[Ir(dppe)_2]PF_6$ (0.10 g, 88 μmol) until a color change from orange to light yellow was complete. The solution was evaporated to dryness, and the residue was metathesized to the PF_6^- salt by using the procedure described for $[IrCO(dppe)_2]PF_6$. The solids were dissolved in (1:1 v/v) MeOH–CH_2Cl_2 (20 mL), followed by concentration of the solution in vacuo and cooling to −25 °C. Filtration afforded 65 mg (60%) of light yellow powder. IR ($CHCl_3$): ν_{MH} = 2132 (w) cm^{-1}.

***trans*-$[IrCl(SCH_3)(dppe)_2]PF_6$.** A stirred CH_2Cl_2 solution (50 mL) of $[Ir(dppe)_2]PF_6$ (0.85 g, 0.75 mmol) was titrated by dropwise addition of a CH_2Cl_2 solution (15 mL) containing a 1 molar excess of CH_3SCl ($d \approx 1.24$ g/mL^3). When the color change from orange to light yellow-orange was complete, the reaction solution was evaporated to dryness. At this stage, the 360-MHz ^1H NMR spectrum of the crude product indicated ca. 35% *cis*-$[IrCl_2(dppe)_2]^+$ and ca. 40% *trans*-$[IrCl(SCH_3)(dppe)_2]^+$. The crude reaction product slurried in CH_2Cl_2 (20 mL) was cooled to −25 °C. Filtration of this cold slurry afforded a 28% yield (0.25 g) of pure white *cis*-$[IrCl_2(dppe)_2]PF_6{\cdot}{}^1/_4CH_2Cl_2$,[27] which was washed with $CHCl_3$ and dried. The combined filtrate was evaporated to dryness and extracted with $CHCl_3$; then the extract was cooled to −25 °C and filtered. In this way, two crops of pure *trans*-$[IrCl(SCH_3)(dppe)_2]PF_6$ were obtained. Yield: 26% (0.24 g) of orange-yellow needles. ^{31}P NMR [(5:1 v/v) CH_2Cl_2–C_6D_6]: −3.1 ppm (s).

For *cis*-$[IrCl_2(dppe)_2]PF_6{\cdot}{}^1/_4CH_2Cl_2$, ^{31}P NMR (5:1 v/v CH_2Cl_2–C_6D_6): −0.4 (pseudotriplet), −3.8 ppm (pseudotriplet).[28]

Results and Discussion

Alkylation and Protonation of $[Ir(E_2)(dppe)_2]^+$ (E = S, Se). The reactions of coordinated dichalcogenides with electrophiles have been reported for a number of complexes, and not unexpectedly, the facility of these processes is strongly dependent on the basicity of the metal center and the overall charge of the complex. At one extreme, Treichel and Werber have shown that in $(C_5H_5)_2Nb(S_2)Cl$ the η^2-S_2 unit can be alkylated with CH_3I to give $(C_5H_5)_2NbI_2Cl$ and $(CH_3)_2S_2$.[29]

---

(22) Teo, B.-K.; Ginsberg, A. P.; Calabrese, J. C. *J. Am. Chem. Soc.* **1976**, *98*, 3027.

(23) Vaska, L.; Catone, D. L. *J. Am. Chem. Soc.* **1966**, *88*, 5324. Sacco, A.; Rossi, M.; Nobile, C. F. *Chem. Commun.* **1966**, 589. The procedure described by Vaska gives approximately 5% $Ir(dppe)_2H$, apparently due to presence of alcohol in the decarbonylation solvent. Complete decarbonylation of $[IrCO(dppe)_2]Cl$ by either procedure is difficult.

(24) For a further discussion of this synthetic method, see: Bolinger, C. M.; Hoots, J. E.; Rauchfuss, T. B. *Organometallics* **1982**, *1*, 223.

(25) Ainscough, E. W.; Brodie, A. M.; Furness, A. R. *J. Chem. Soc., Dalton Trans.* **1973**, 2360.

(26) Schmidpeter, A.; Brecht, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1969**, *24B*, 179.

(27) Miller, J. S.; Caulton, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 1067.

(28) Our ^{31}P NMR results differ significantly from those presented in ref 27.

(29) Treichel, P. M.; Werber, G. P. *J. Am. Chem. Soc.* **1968**, *90*, 1753.

Table II. ^1H NMR Spectroscopic Data for $[Ir(dppe)_2LL']^{n+}$ Complexes[a]

	^1H NMR, δ				
complex	ortho phenyl (high field)[b]	CH_2CH_2[b]	ECH_3	other	solvent
$[Ir(S_2)(dppe)_2]^+$	6.02 (3.9 H)	2.0–3.0			$CDCl_3$
$[Ir(S_2CH_3)(dppe)_2]^{2+}$ (Λ,*S*), (Δ,*R*)	6.03 (1.9 H), 6.80 (2.0 H)	2.0–3.4	2.35 d (2.8 H)		CD_3NO_2
(Λ,*R*), (Δ,*S*)	6.22 (0.1 H), 6.87 (0.1 H)	2.0–3.4	1.60 d (0.14 H)		CD_3NO_2
$[Ir(S_2H)(dppe)_2]^{2+}$	6.20 (3.6 H)	2.2–3.1			$CDCl_3$
$[Ir(SCH_3)(SCN)(dppe)_2]^+$	6.27 (1.7 H), 6.19 (1.8 H)	2.6–3.7	−0.34 d		$CDCl_3$/ CD_3NO_2
$[Ir(SCH_3)(CNCH_3)(dppe)_2]^{2+}$	6.33 (1.7 H), 6.50 (1.8 H)	2.6–4.0	0.05 d	3.69 b s ($CNCH_3$, 3 H)	CD_3NO_2
trans-$[Ir(SCH_3)Cl(dppe)_2]^+$		3.10 pt	−0.03 s		CD_3NO_2
trans-$[Ir(SCH_3)H(dppe)_2]^+$		2.81, 2.40	0.30 s	−14.81 q (MH)	$CDCl_3$
$[Ir(Se_2)(dppe)_2]^+$	6.14 (3.8 H)	2.2–2.8			$CDCl_3$
$[Ir(Se_2CH_3)(dppe)_2]^{2+}$ (Λ,*S*), (Δ,*R*)	6.48 (1.5 H), 6.26 (1.5 H)	2.1–3.2	2.04 d (2 H)		$CDCl_3$/ CD_2Cl_2
(Λ,*R*), (Δ,*S*)	6.61 (0.25 H), 6.17 (0.25 H)	2.1–3.2	1.29 d (0.4 H)		$CDCl_3$/ CD_2Cl_2
$[Ir(Se_2H)(dppe)_2]^{2+}$	6.24 (3.2 H)[c]	2.3–3.5			$CDCl_3$
$[Ir(Cl_2)(dppe)_2]^+$	6.71 (3.8 H)	2.9–3.5			CD_3NO_2

[a] Orientation of LL′ is cis, unless otherwise indicated. Peak multiplicity: s = singlet, d = doublet, pt = pseudotriplet, q = quintet, b = broadened. All doublets arise from $^4J_{PH}$ ~ 6 Hz and the quintet from $^2J_{PH}$ = 13 Hz. [b] Integrations are determined by comparison with the phenyl region (40 H). All complexes show normal, complex phenyl H multiplets (36 H) between ~6.8 and 8.2 ppm. Each ortho phenyl H resonance (2 H or 4 H) is an overlapping doublet of doublets (pseudotriplet) with $^3J_{PH}$ ~ 8–9 Hz and $^3J_{HH}$ ~ 8 Hz. The dppe backbone occurs as complex multiplets (8 H), unless otherwise indicated. [c] Ortho phenyl H integration was low due to slow decomposition of the complex.

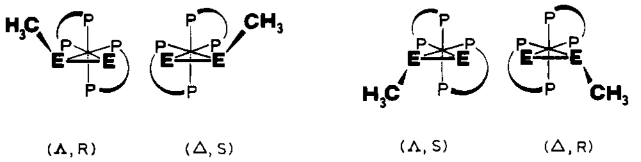


Figure 1. Perspective views of the four stereoisomers of $[Ir(E_2R)(dppe)_2]^{2+}$. The (Λ,*S*), (Δ,*R*) pair is proposed to predominate in solution.

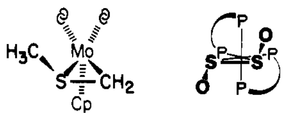


Figure 2. Perspective views of the coordination spheres of $(C_5H_5)Mo(CO)_2(\pi\text{-}CH_2SCH_3)$ and $[Ir(S_2O_2)(dppe)_2]^+$.

In contrast, other workers have established that powerful reagents such as RSO_3CH_3 (R = F, CF_3) are required to alkylate disulfur complexes of Os(II) and Ir(III). At room temperature and with use of $CF_3SO_3CH_3$, alkylation of neutral complexes of $Os(E_2)(CO)_2(PPh_3)_2$ (E = S, Se) is immediate,[15b,30] while $[Ir(S_2)(dppe)_2]^+$ requires reaction times of several days.[4] The $[Ir(Se_2)(dppe)_2]^+$ complex was found to alkylate approximately twice as fast as the analogous sulfur compound. This is in accord with the greater nucleophilicity of coordinated selenium ligands. The $[Ir(Se_2CH_3)(dppe)_2](PF_6)_2$ complex was isolated as a stable, red crystalline product, which, like the S_2CH_3 complex, is quite stable in solution.[31]

In the preparation of $[Ir(S_2CH_3)(dppe)_2](PF_6)_2$, the use of gel-permeation chromatography to purify the complex gave interesting results. Not only was the desired S_2CH_3 dicationic complex separated from gross impurities but efficient separation from the S_2 monocationic complex was also achieved. The basis of this separation is probably related to relative sizes of the respective ion-paired complexes.

For the complexes $[Ir(E_2CH_3)(dppe)_2]^{2+}$ (E = S, Se), the geometry of the alkylated chalcogenide atom is assumed to be pyramidal as is observed crystallographically for $[Os(\eta^2\text{-}S_2CH_3)(CO)_2(PPh_3)_2]ClO_4$.[5] Thus, it appears as if the alkylated chalcogenide atom resembles other three-coordinate compounds like the trialkylsulfonium ions (R_3S^+) and organic sulfoxides and selenoxides.[32] In the case of the iridium complexes, two diastereoisomers are possible depending on the disposition of the methyl group relative to the dppe chelate rings (Figure 1). On the basis of steric considerations, we predict that the (Λ,*S*), (Δ,*R*) enantiomeric pair will predominate. Consistent with this view, we note that the solid-state structure of $(C_5H_5)Mo(CO)_2(\pi\text{-}CH_2SCH_3)$ reveals a pyramidal sulfur whose methyl substituent is orientated away from the sterically more imposing C_5H_5 ligand (Figure 2).[33]

Careful inspection of the ^1H NMR spectra of $[Ir(E_2CH_3)(dppe)_2](PF_6)_2$ (E = Se, S) (Table II, Figure 3) reveals the presence of *both* diastereomers in a ratio of ~6:1 (Se) and ~20:1 (S). Like the major diastereoisomer, the minor isomer is characterized by a ^{31}P-coupled E–CH_3 doublet and two sets of high-field shifted ortho phenyl protons, the latter being characteristic of *cis*-$[Ir(X)(Y)(dppe)_2]^{n+}$ complexes.[34] The steric bulk of the substituent and its distance from the $Ir(dppe)_2$ moiety are expected to influence the major:minor diastereoisomer ratio, [(Δ,*R*) + (Λ,*S*)]/[(Δ,*S*) + (Λ,*R*)]. For both complexes, the isomer ratio is invariant from preparation to preparation and does not change when the complex is heated to 70 °C for 2 h or allowed to stand in solution for long periods of time. We conclude therefore that the observed isomer ratio reflects their relative thermodynamic stabilities and is *not* a result of stereoselectivity in the methylation step. A variable-temperature ^1H NMR study of $[Ir(Se_2CH_3)(dppe)_2](PF_6)_2$ confirmed its nonrigid character. In CD_3NO_2 solution, the Se_2CH_3 and high-field ortho phenyl proton resonances had significantly broadened at 50 °C; at 80 °C the resonances for minor diastereoisomer had disappeared and the Se_2CH_3 absorption had almost completely collapsed. A limiting high-temperature spectrum was not observed due to the thermal decomposition of the complex. Similar behavior was seen in the analogous S_2CH_3 compound.

Protonation of $[Ir(E_2)(dppe)_2]^+$ (E = S, Se) provides an interesting supplement to the alkylation studies.[35] While the

---

(30) Clark, G. R.; Russell, D. R.; Roper, W. R.; Walker, A. *J. Organomet. Chem.* **1977**, *136*, C1.

(31) Attempts to prepare $[Ir(dppe)_2(O_2R)](PF_6)_2$ (R = CH_3, H) by similar methods produced decomposition.

(32) Mikolajczyk, M.; Drabowicz, J. *Top. Stereochem.* **1982**, *13*, 333 ff.

(33) de Gil, E. R.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 3751.

(34) Ginsberg, A. P.; Lindsell, W. E. *Inorg. Chem.* **1973**, *12*, 1983. Chatt, J.; Pombeiro, A. J. L.; Richards, R. L. *J. Organomet.* Chem. **1980**, *184*, 357.

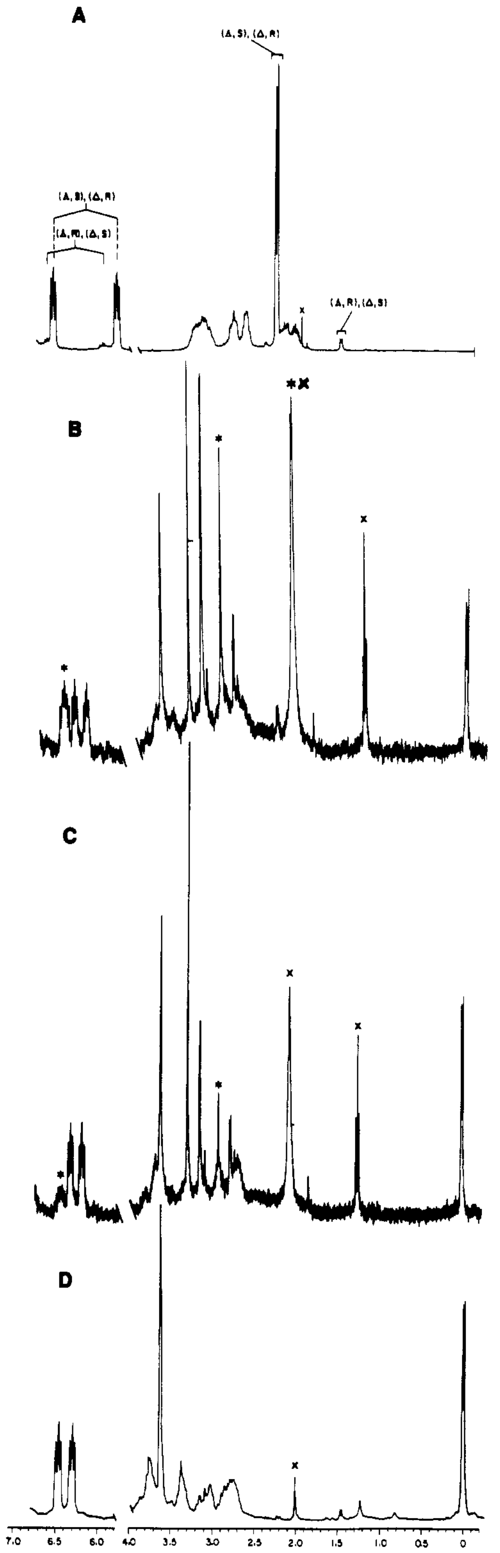


Figure 3. ^{1}H NMR spectra (360 MHz) of four stages of the reaction of $[Ir(S_2CH_3)(dppe)_2]^{2+}$ (1) with CH_3NC (see eq 5) in CD_3NO_2 solution. Spectrum A is that of 1 with the proposed stereochemical assignments of the diastereotopic resonances indicated. Spectra B and C were recorded 20 and 50 min, respectively, after the addition of 2.2 equiv of CH_3NC to a 8×10^{-2} M CD_3NO_2 solution of 1; signals marked with an asterisk arise from the intermediate (see text) while those marked with an × are from solvent impurities in the reaction: CH_3CH_2OH (1.21 ppm) and H_2O (~2.06 ppm). Spectrum B contains approximately equal concentrations of CH_3NC (3.13 ppm), CH_3NCS (3.28 ppm), the intermediate $1{\cdot}CH_3NC$, and the final product. Spectrum D is that of purified $[Ir(SCH_3)(CH_3NC)(dppe)_2](PF_6)_2$.

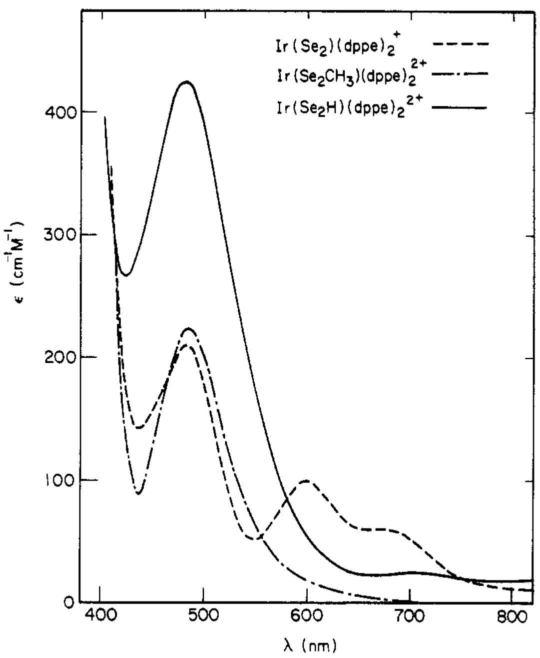


Figure 4. Optical absorption spectra of $[Ir(Se_2)(dppe)_2]Cl$, $[Ir(Se_2CH_3)(dppe)_2](PF_6)_2$, and $[Ir(Se_2H)(dppe)_2]^{2+}$. The extinction coefficients for $[Ir(Se_2H)(dppe)_2]^{2+}$ are unreliable due to the slight turbidity of its solutions. (The solvents used are indicated in Table II.)

protonation products were not isolated, the spectroscopic characteristics of the species in solution leave little doubt as to their identity. Protonations with strong acids (CF_3SO_3H) are rapid and are accompanied by significant changes in the visible spectra, which are very similar to those produced by alkylation (Table III). The compound $[Ir(\eta^2\text{-}S_2H)(dppe)_2]^{2+}$ is stable in solution, and spectrophotometric measurements establish that the protonation–deprotonation cycle can be repeated several times without significant decomposition. The acidity of this dicationic complex is obviously considerable since its formation requires the use of CF_3SO_3H[36] and it can be completely deprotonated with methanol. A variable-temperature ^{1}H NMR study of $[Ir(\eta^2\text{-}S_2H)(dppe)_2]^{2+}$ provided supporting evidence for the presence of the η^2-hydroperthiolate ligand. At 45 °C, the high-field ortho phenyl proton resonance consists of a single broadened pseudotriplet, consistent with a relatively fast proton exchange. When the solution is cooled to −78 °C, the spectrum goes through a series of changes which eventually results in four separate, broadened ortho phenyl resonances. This behavior is consistent with the presence of both diastereoisomers and is analogous to the S_2CH_3 case (vide supra). Integration of the peaks indicated that the two diastereoisomers were present in an ~3:2 ratio.

$[Ir(\eta^2\text{-}Se_2)(dppe)_2]^+$ is more basic than its sulfur analogue since it is fully protonated by smaller quantities of CF_3CO_2H. $[Ir(Se_2)(dppe)_2]^+$ is green, while the protonated product, like $[Ir(Se_2CH_3)(dppe)_2]^{2+}$, is orange (Figure 4).

Reactions of $[Ir(S_2CH_3)(dppe)_2]^{2+}$ with Nucleophiles. Solutions of $[Ir(S_2CH_3)(dppe)_2]^{2+}$ (1) react very quickly with 2 equiv of $(CH_3)_2PhP$ to give equal amounts of $[Ir(dppe)_2]^+$, $(CH_3)_2PhPS$, and the phosphonium ion $(CH_3)_2PhPSCH_3^+$. The reaction proceeds cleanly, and the nature of the products were readily determined by 360-MHz ^{1}H NMR spectroscopy. Particularly distinctive are the two methyl doublets, in a 2:1 ratio by integration, for the unusual phosphonium ion. When

---

(35) Adzamli, I. K.; Nosco, D. L.; Deutsch, E. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1364.

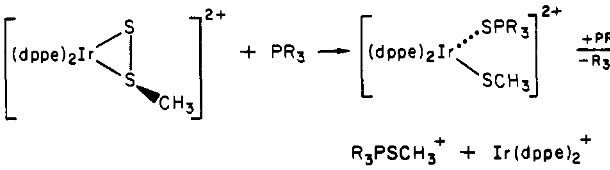
(36) Approximately 2000 equiv of CF_3CO_2H was required for 75% protonation as determined by optical spectroscopy. Initial concentration of complex was 9×10^{-4} M.

Table III. Electronic and Mass Spectral Data for $[Ir(dppe)_2LL']^{n+}$ Complexes

complex[a]	visible (400-800 nm) λ_{max}, nm (ϵ M^{-1} cm^{-1})	visible (400-800 nm) solvent, color	MS *m/e*[b] (intens[c])	MS comments[f]
$[Ir(S_2)(dppe)_2]Cl$	460 (178), 526 (sh, ~70)	MeOH, orange-red	1053 (7)	FD
			1053 (10)	FAB
$[Ir(S_2CH_3)(dppe)_2](PF_6)_2$	419 (480)	CH_2Cl_2, yellow	534[d] (147)	FD
$[Ir(S_2H)(dppe)_2]^{2+}$	402 (sh)	$CHCl_3$, pale yellow		
$[Ir(SCH_3)(SCN)(dppe)_2](PF_6)_2$			no M^+	FD
$[Ir(SCH_3)(CH_3NC)(dppe)_2](PF_6)_2$			538.5 (400)[d]	FD
trans-$[Ir(SCH_3)Cl(dppe)_2](PF_6)_2$	420 (~530), 450 (sh, ~460)	CH_2Cl_2, orange	1071 (300), 535.5 (670)[d]	FD
trans-$[Ir(SCH_3)H(dppe)_2](PF_6)_2$			no M^+	FD
$[Ir(Se_2)(dppe)_2]Cl$	482 (209), 600 (90), 674 (sh, ~50)	MeOH, green	1147 (2)	FD
			1148 (3)[e]	FAB
$[Ir(Se_2CH_3)(dppe)_2](PF_6)_2$	484 (235)	CH_2Cl_2, red-orange	no M^+	
$[Ir(Se_2H)(dppe)_2]^{2+}$	484	$CHCl_3$, pink-orange		
$[Ir(Cl_2)(dppe)_2]PF_6$			1059 (500)	FD
			1059 (6)	FAB

[a] Stereochemistry of the complexes are cis unless noted otherwise. [b] For molecular ion (M^+) unless noted otherwise. [c] Relative to the most abundant $[Ir(dppe)_2]^+$ isotopomer: *m/e* 989 (intensity 100). [d] M^{2+}. [e] $(MH)^+$. [f] FD is field desorption and FAB is fast-atom bombardment.

the reaction is allowed to proceed only halfway by the addition of only 1 equiv of $(CH_3)_2PhP$, ^1H NMR spectroscopy reveals that equal amounts of $[Ir(dppe)_2]^+$, $(CH_3)_2PhPS$, and $(CH_3)_2PhP(SCH_3)^+$ are again obtained. Apparently after one phosphine abstracts a sulfur atom, a rapid reaction ensues whereby a second phosphine becomes quarternized by the SCH_3^+ moiety. Completely analogous results were obtained by using PPh_3 as a nucleophile, and again the reaction is quick and clean. A mechanistic scenario that conforms to the observed product distribution is depicted in eq 4.

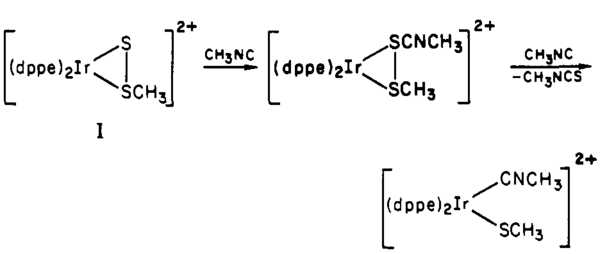


(4)

In contrast to the facility of S atom transfer from the S_2CH_3 complex, we and others find that $[Ir(S_2)(dppe)_2]^+$ does not react with PPh_3.[4] Ginsberg and co-workers found that the more nucleophilic phosphine $EtPh_2P$ consumed ca. 30% $[Ir(S_2)(dppe)_2]^+$ in 12 days at 25 °C;[21] under comparable conditions we find that the reaction of the S_2CH_3 complex with PPh_3 is 2.5 × 10^4 times faster.

Solutions of **1** react with 2 equiv of CH_3NC to give *cis*-$[Ir(SCH_3)(CH_3NC)(dppe)_2]^{2+}$ and CH_3NCS. The identity of the latter was confirmed both by ^1H NMR spectroscopy and by gas chromatographic comparisons with an authentic sample. The new iridium(III) product, *cis*-$[Ir(SCH_3)(CH_3NC)(dppe)_2]^{2+}$, showed a characteristically intense ν_{NC} band in its IR spectrum and two equally intense ^1H NMR absorptions at 3.69 and 0.05 ppm (J_{PH} = 6 Hz), attributable to the CH_3NC and SCH_3 groups, respectively. The cis geometry of this complex was indicated by the observation of two sets of high-field ortho phenyl resonances. It is interesting to note that CH_3NC does *not* react with elemental sulfur even in benzene (80 °C, 24 h); it is therefore obvious that **1** is an especially electrophilic sulfur-transfer reagent.

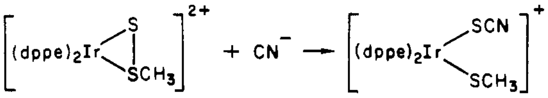
When **1** is treated with a deficiency of CH_3NC in CD_3NO_2, four species are detectable by 360-MHz ^1H NMR: unreacted **1**, equal amounts of *cis*-$[Ir(SCH_3)(CH_3NC)(dppe)_2]^{2+}$ and CH_3NCS, and an intermediate that appears to be the adduct **1**·CH_3NC. Like the final product, this adduct displays ^1H NMR absorptions for reacted CH_3NC, two sets of high-field ortho phenyl hydrogens, and a ^{31}P-coupled SCH_3 doublet (Figure 3). Importantly, the chemical shift of this SCH_3 doublet more closely resembles that in **1** than that of any simple, monodentate SCH_3 derivative of the $Ir(dppe)_2$ moiety (vide infra).[37] We propose that **1**·CH_3NC possesses the structure depicted in eq 5 on the basis of (i) its formula



(5)

(deduced from the stoichiometry and corroborated by NMR intensities), (ii) its ^1H NMR properties (Figure 3), and (iii) its further reaction with CH_3NC to give equal amounts of *cis*-$[Ir(SCH_3)(CH_3NC)(dppe)_2]^{2+}$ and CH_3NCS. It is important to note that the SCH_3 ^1H NMR chemical shift of the intermediate is ca. 2 ppm downfield of the distinctive and narrow region (±0.3 ppm vs. Me_4Si) observed for other compounds of the type $[IrX(SCH_3)(dppe)_2]^{z+}$ (vide infra). For this reason we suggest that the S–S bond is retained in the intermediate. Comparison of this reaction pathway with that proposed for the oxygen atom transfer involving transition-metal hydroperoxide complexes (eq 3) reveals obvious similarities. Also of potential relevance to this reaction is the observation that CH_3NCS has been shown to react with low-valent metal complexes to give dithiocarbonimidate and isocyanide type ligands.[38]

Solutions of **1** react with 1 equiv of CN^- to give *cis*-$[Ir(SCH_3)(SCN)(dppe)_2]^+$ (eq 6), which was isolated as pale



(6)

yellow crystals of its PF_6^- salt. The product was characterized by elemental analysis and ^1H NMR and IR spectroscopy. In its 360-MHz ^1H NMR spectrum, absorptions attributable to two sets of ortho phenyl protons were observed, thereby confirming the cis stereochemistry of the complex. Furthermore, the SCH_3 resonance is a doublet at −0.34 ppm (*upfield* of $(CH_3)_4Si$) with J_{PH} = 6 Hz. The presence of the S-bound SCN^- ligand is suggested by the observed ν_{CN} absorption at 2100 cm^{-1} (cf. *trans*-$[Ir(SCN)_2(dppe)_2]^+$, ν_{CN} = 2108 cm^{-1} [39]).

---

(37) Analogous results were obtained in the reaction of $[Ir(dppe)_2(Se_2CH_3)](PF_6)_2$ and CH_3NC.

(38) Harris, R. O.; Powell, J.; Walker, A.; Yaneff, P. V. *J. Organomet. Chem.* **1977**, *141*, 217. See also: Miller, D. J.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1980**, *102*, 4925.

The S-bound isomer is expected on kinetic grounds.[40]

Studies of [IrX(SCH_3)(dppe)$_2$]PF_6 (X = H, Cl). In view of the self-consistent nature of the associated spectroscopic and analytical data, there can be little doubt that the new compounds *cis*-[Ir(SCH_3)(SCN)(dppe)$_2$]PF_6 and *cis*-[Ir(SCH_3)(CH_3NC)(dppe)$_2$](PF_6)$_2$ are correctly formulated. Nonetheless, the ^1H NMR shifts assigned to the SCH_3 resonances occurred at unexpectedly high field (Table II). Evaluation of these NMR data is difficult because few monomeric 18e SCH_3 complexes exist, and for this reason we prepared two new SCH_3 derivatives of the Ir^{III}(dppe)$_2$ moiety.

Orange solutions of [Ir(dppe)$_2$]PF_6 slowly assume a pale yellow color upon exposure to an excess of CH_3SH. The major product of this reaction is [IrH(SCH_3)(dppe)$_2$]$^+$, which was isolated in crystalline form as its PF_6^- salt. Its IR spectrum revealed a weak absorption at 2130 cm^{-1}, assigned as ν_{IrH}. This thiolato–hydride complex possesses trans stereochemistry as established by NMR spectroscopy. In its 360-MHz ^1H NMR spectrum, the hydride appears as a quintet at −14.8 ppm ($^2J_{PH}$ = 13 Hz) resulting from coupling to four equivalent cis phosphorus atoms, there are no high-field shifted ortho phenyl resonances,[34] and notably, the singlet for the S–CH_3 group appears at 0.30 ppm. Variable-temperature ^1H NMR spectroscopy (to −80 °C) at 360 MHz gave little evidence to support the idea of fluxional character in the molecule.

The reaction of CH_3SCl with solutions of [Ir(dppe)$_2$$PF_6$ gives principally *trans*-[IrCl(SCH_3)(dppe)$_2$]$^+$ and *cis*-[$IrCl_2$(dppe)$_2$]$^+$, which were separated by fractional crystallization of their PF_6^- salts. The stereochemistry assigned to *trans*-[IrCl(SCH_3)(dppe)$_2$]$^+$ follows from its ^1H NMR properties; notably, the absence of any high-field shifted ortho phenyl resonances,[34] the simple pattern for the dppe backbone, the lack of any ^{31}P coupling to the SCH_3 resonance, and variable-temperature ^1H NMR results were very similar to those obtained with the hydrido-methanethiolato complex. The SCH_3 absorption at −0.07 ppm is in the region observed for other complexes of the type [IrX(SCH_3)(dppe)$_2$]$^{n+}$, where X = CH_3NC, SCN, and H.

Conclusions

Alkylation and protonation of [Ir(E_2)(dppe)$_2$]$^+$ have been shown to lead to a mixture of the two possible diastereomers of [Ir(E_2R)(dppe)$_2$]$^{2+}$ (E = S, Se; R = H, CH_3). In the case of the E_2CH_3 complexes, the diastereoisomer ratio is an equilibrium mixture as ^1H NMR spectroscopy indicated the onset of fluxionality at only slightly elevated temperatures. Although complexes of the η^2-E_2CH_3 moiety were previously known,[4,30] this is the first report describing examples of η^2-E_2H ligands. In both the alkylation and protonation reactions, the Se_2 ligand was decidedly more nucleophilic and more basic than the S_2 ligand. This finding is consistent with the recent molecular orbital calculations on [Ir(E_2)(PH_3)$_4$]$^+$ (E = S, Se).[41]

The most important findings of this project were the determination of the order of sulfur-transfer reactivity, [Ir(S_2CH_3)(dppe)$_2$]$^{2+}$ > *c*-S_8 > [Ir(S_2)(dppe)$_2$]$^+$, and the elucidation of the associated reactivity patterns. This ranking was deduced from the reactivities of the respective compounds with CH_3NC, CN^-, and tertiary phosphines. Since these thiophilic reagents function as strong nucleophiles,[42] electrophilicity of the S_2 ligand in [Ir(S_2)(dppe)$_2$]$^+$ must be quite modest. The reactions of the η^2-S_2R unit with thiophiles were found to follow three pathways: (i) If NuS is a good ligand, it remained coordinated and no further reaction ensued (e.g., Nu = CN^-; eq 6). (ii) If NuS is a poor ligand and Nu is a good ligand, NuS was eliminated and Nu and SCH_3 remained coordinated (e.g., Nu = CH_3NC; eq 5). (iii) In the event that Nu, NuS, and $NuSCH_3^+$ were poor ligands (or ligand precursors) for [Ir(dppe)$_2$]$^+$, then NuS, $NuSCH_3^+$, and [Ir(dppe)$_2$]$^+$ were produced (e.g., Nu = PPh_3; eq 4). The most electrophilic site in these E_2R complexes is clearly the nonalkylated chalcogenide. Its enhanced reactivity can be appreciated by noting that *c*-S_8 does not react with CH_3NC at 80 °C while [Ir(S_2CH_3)(dppe)$_2$]$^{2+}$ does so rapidly at 20 °C.

Acknowledgment. This research was supported by the National Science Foundation (Grant No. CHE 81-06781). We also acknowledge partial support by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank Englehard Industries for a loan of iridium trichloride. T.B.R. is a recipient of a Camille and Henry Dreyfus Teacher-Scholar Grant.

Registry No. **1**·2PF_6, 71393-33-4; [IrCO(dppe)$_2$]Cl, 15308-58-4; [IrCO(dppe)$_2$]PF_6, 86561-51-5; *trans*-IrCl(CO)(PPh_3)$_2$, 15318-31-7; [Ir(dppe)$_2$]Cl, 15390-38-2; Cp_2TiSe_5, 12307-22-1; IrH(dppe)$_2$, 29189-86-4; [Ir(Se_2)(dppe)$_2$]Cl, 40603-51-8; [Ir(η^2-Se_2CH_3)(dppe)$_2$](PF_6)$_2$, 86542-53-2; *cis*-[Ir(SCH_3)(CH_3NC)(dppe)$_2$](PF_6)$_2$, 86528-96-3; *cis*-[Ir(SCH_3)(SCN)(dppe)$_2$]PF_6, 86528-98-5; [(CH_3)$_2$PhPSCH$_3$]PF_6, 86528-99-6; (CH_3)$_2$PhPS, 1707-00-2; *trans*-[IrH(SCH_3)(dppe)$_2$]PF_6, 86529-01-3; [Ir(dppe)$_2$]PF_6, 41047-09-0; *trans*-[IrCl(SCH_3)(dppe)$_2$]PF_6, 86529-03-5; *cis*-[$IrCl_2$(dppe)$_2$]PF_6, 86529-05-7; [Ir(S_2)(dppe)$_2$]$^+$, 40603-50-7; [Ir(S_2H)(dppe)$_2$]$^{2+}$, 86542-54-3; [Ir(Se_2H)(dppe)$_2$]$^{2+}$, 86529-06-8; Se_2, 12185-17-0; S_2, 23550-45-0; CN^-, 57-12-5.

---

(39) Faraone, F.; Sergi, S. *J. Organomet. Chem.* **1976**, *112*, 201.

(40) Burmeister, J. L. "Chemistry and Biochemistry of Thiocyanic Acid and its Derivatives"; Newman, A. A., Ed.; Academic Press: London, 1975; Chapter 2.

(41) Ginsberg, A. P.; Osborne, J. H.; Sprinkle, C. R. *Inorg. Chem.* **1983**, *22*, 254.

(42) Davis, R. E. *Surv. Prog. Chem.* **1964**, *2*, 189–238.