Insertion of CO_2, CS_2, and COS into Iron(II)−Hydride Bonds

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The reactions between *cis*-Fe(dmpe)$_2$H$_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$) (**1**) or *cis*-Fe(PP$_3$)H$_2$ (PP$_3$ = P($CH_2CH_2PMe_2$)$_3$) (**2**) and carbon dioxide (CO_2), carbon disulfide (CS_2), and carbonyl sulfide (COS) are investigated. At 300 K, additions of CO_2 (1 atm), CS_2 (2 equiv), and COS (1 atm) to **1** result in the formation of a stable *trans*-formato hydride, *trans*-Fe(dmpe)$_2$(OCHO)H (**3a**), a *trans*-dithioformato hydride, *trans*-Fe(dmpe)$_2$(SCHS)H (**4a**), and a *trans*-thioformato hydride, *trans*-Fe(dmpe)$_2$(SCHO)H (**5a**), respectively. When CS_2 and COS are added to *cis*-Fe(dmpe)$_2$H$_2$ at 195 K, a *cis*-dithioformato hydride, **4b**, and a *cis*-thioformato hydride, **5b**, respectively, are observed as the initially formed products, but there is no evidence of the corresponding *cis*-formato hydride upon addition of CO_2 to *cis*-Fe(dmpe)$_2$H$_2$. Additions of excess CO_2, CS_2, and COS to **1** at lower temperatures (195−240 K) result in the formation of a *trans*-bis(formate), *trans*-Fe(dmpe)$_2$(OCHO)$_2$ (**3b**), a *trans*-bis(dithioformate), *trans*-Fe(dmpe)$_2$(SCHS)$_2$ (**4c**), and a *cis*-bis(thioformate), *cis*-Fe(dmpe)$_2$(SCHO)$_2$ (**5c**), respectively. *trans*-Fe(dmpe)$_2$(SCHO)$_2$ (**5d**) is prepared by the addition of excess COS at 300 K. Additions of CO_2 (1 atm), CS_2 (0.75 equiv), and COS (1 atm) to **2** at 300 K result in the formation of a thermally stable, geometrically constrained *cis*-formato hydride, *cis*-Fe(PP$_3$)(OCHO)H (**6a**), a *cis*-dithioformato hydride, *cis*-Fe(PP$_3$)(SCHS)H (**7a**), and a *cis*-thioformato hydride, *cis*-Fe(PP$_3$)(SCHO)H (**8a**), respectively. Additions of excess CO_2 and COS to **2** yield a *cis*-bis(formate), *cis*-Fe(PP$_3$)(OCHO)$_2$ (**6b**), and a thermally stable *cis*-bis(thioformate), *cis*-Fe(PP$_3$)(SCHO)$_2$ (**8b**), respectively. All complexes are characterized by multinuclear NMR spectroscopy, with IR spectroscopy and elemental analyses confirming structures of thermally stable complexes where possible. Complexes **3b** and **5a** are also characterized by X-ray crystallography.

Introduction

Insertion of small unsaturated organic molecules such as CO_2 into metal−carbon and metal−hydride bonds is an important chemical step in functionalizing these molecules.[1] The activation and potential catalytic functionalization of CO_2 by transition metal centers have received much recent attention because of its potential as an abundant and inexpensive source of carbon. Furthermore, the development of practical methods for the regeneration of organic compounds from CO_2 is essential in the future management of this greenhouse gas. Reaction between carbon dioxide and metal hydrides has been observed for many transition metal systems,[1−10] particularly the catalytically active platinum group metals. Perutz and co-workers[4] observed the formation of stable formato and bis(formato) complexes from the reaction of CO_2 with Ru(dmpe)$_2$H$_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$). To date, there have been very few examples of the reaction of CO_2 with iron complexes[11,12] and there has been no (or very little) characterization of the resulting insertion products.

In this paper, we report insertion of carbon dioxide, carbon disulfide, and carbonyl sulfide into the iron(II)−hydride bonds of the related iron phosphine complexes *cis*-Fe(dmpe)$_2$H$_2$ (**1**) and *cis*-Fe(PP$_3$)H$_2$ (PP$_3$ = P($CH_2CH_2PMe_2$)$_3$) (**2**), both at 300 K and at low temperature.

Experimental Section

General Information. All manipulations were carried out using standard Schlenk, high-vacuum, and glovebox techniques. Air-sensitive NMR samples were prepared in a nitrogen- or argon-filled glovebox, with solvent vacuum-transferred into an NMR tube fitted with a concentric Teflon valve.[13] Toluene-d_8, tetrahydrofuran-d_8, and benzene-d_6 were dried over sodium/benzophenone and vacuum-distilled immediately prior to use. Ether, hexane, and benzene were dried over sodium wire before distillation under nitrogen from sodium/benzophenone. All compressed gases were obtained from the British Oxygen Co. (BOC gases). Argon (>99.99%), nitrogen (>99.5%), carbon dioxide (>99.995%), and carbonyl sulfide (>97.5%) were used as supplied without further purification. Carbon disulfide was obtained

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from Ajax Chemicals and distilled prior to use. The syntheses of *cis*-$Fe(dmpe)_2H_2$ (**1**)[14] and *cis*-$Fe(PP_3)H_2$ (**2**)[15] have been described elsewhere.

^1H, ^{31}P, and ^{13}C NMR spectra were recorded on a Bruker DRX400 NMR spectrometer at 400.2, 162.0, and 100.6 MHz, respectively, and referenced as follows. ^1H: residual toluene-d_7 at δ 2.09, tetrahydrofuran-d_7 at δ 3.58, and benzene-d_5 at δ 7.15. ^{31}P: external neat trimethyl phosphite at δ 140.85. ^{13}C: toluene-d_8 at δ 20.4, tetrahydrofuran-d_8 at δ 67.4, and benzene-d_6 at δ 128.0. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrometer, the samples being recorded as Nujol mulls with NaCl plates. Elemental analyses were carried out at the Campbell Microanalytical Laboratory, University of Otago, New Zealand.

[OC-6-11]-Bis(1,2-bis(dimethylphosphino)ethane)(formato)-hydridoiron(II), *trans*-$Fe(dmpe)_2(OCHO)H$ (3a). CO_2 (1 atm) was added at 300 K to an NMR tube containing a degassed solution of *cis*-$Fe(dmpe)_2H_2$ (**1**) (30 mg, 0.084 mmol) in tetrahydrofuran-d_8 (0.5 mL). NMR spectroscopy indicated quantitative formation of **3a**. The solvent was removed, the residue was extracted into benzene, and the extract was filtered. Removal of benzene and recrystallization from ether gave **3a** as an orange crystalline solid in analytically pure form (26 mg, 77%). Anal. Calcd for $C_{13}H_{34}FeO_2P_4$: C, 38.82; H, 8.46. Found: C, 39.0; H, 8.8. ^1H NMR (tetrahydrofuran-d_8, 300 K): δ −33.96 (p, J_{PH} = 49 Hz, 1H, Fe−*H*), 1.27 (s, 12H, PCH_3), 1.35 (s, 12H, PCH_3), 1.69 (br s, 4H, PCH_2), 2.20 (br s, 4H, PCH_2), 7.78 (s, 1H, OC*H*O). $^{31}P\{^1H\}$: δ 79.1 (s). $^{13}C\{^1H\}$ NMR: δ 15.3 (s, PCH_3), 23.0 (br s, PCH_3), 32.0 (p, J_{CP} = 13 Hz, PCH_2), 168.1 (p, J_{CP} = 95 Hz, OCHO). IR (Nujol; cm^{-1}): 1805 (ν(Fe−H)), 1602 ($\nu_{asym}(CO_2)$), 1328 ($\nu_{sym}(CO_2)$).

[OC-6-11]-Bis(1,2-bis(dimethylphosphino)ethane)bis(formato)-iron(II), *trans*-$Fe(dmpe)_2(OCHO)_2$ (3b). CO_2 (5−6 atm) was added at 195 K to an NMR tube containing a degassed solution of *cis*-$Fe(dmpe)_2H_2$ (**1**) (25 mg, 0.07 mmol) in tetrahydrofuran-d_8 (0.5 mL). Green crystals of **3b** formed from a dark orange solution and were stable at 300 K in suspension. Out of solution, the crystals decomposed within 5−10 min. ^1H NMR (tetrahydrofuran-d_8, 300 K): δ 1.33 (s, 24H, PCH_3), 2.52 (s, 8H, PCH_2), 6.46 (s, 2H, OC*H*O). $^{31}P\{^1H\}$ NMR: δ 69.6 (s). $^{13}C\{^1H\}$ NMR: δ 14.3 (s, PCH_3), 30.5 (p, J_{CP} = 11 Hz, PCH_2), 170.5 (s, OCHO). IR (Nujol; cm^{-1}): 1607 ($\nu_{asym}(CO_2)$), 1322 ($\nu_{sym}(CO_2)$). Green crystals of **3b** suitable for X-ray analysis were grown in tetrahydrofuran-d_8 under 5−6 atm of CO_2 at 273 K.

[OC-6-32]-Bis(1,2-bis(dimethylphosphino)ethane)(dithioformato)-hydridoiron(II), *trans*-$Fe(dmpe)_2(SCHS)H$ (4a). CS_2 (10 μL, 0.17 mmol) was added at 300 K to an NMR tube containing a solution of *cis*-$Fe(dmpe)_2H_2$ (**1**) (30 mg, 0.084 mmol) in tetrahydrofuran-d_8 (0.5 mL) under nitrogen. NMR spectroscopy indicated quantitative formation of **4a**. The solvent was removed, the residue was extracted into benzene, and the extract was filtered. Removal of benzene and recrystallization from ether gave **4a** as a purple crystalline solid (27 mg, 74%). Mp: >280 °C dec. ^1H NMR (tetrahydrofuran-d_8, 300 K): δ −23.29 (p, J_{PH} = 51 Hz, 1H, Fe−*H*), 1.33 (s, 12H, PCH_3), 1.48 (s, 12H, PCH_3), 1.72 (br s, 4H, PCH_2), 2.32 (br s, 4H, PCH_2), 11.66 (s, 1H, SC*H*S). $^{31}P\{^1H\}$ NMR: δ 76.1 (s). $^{13}C\{^1H\}$ NMR: δ 17.6 (s, PCH_3), 24.7 (br s, PCH_3), 32.9 (p, J_{CP} = 14 Hz, PCH_2), 237.6 (s, SCHS). IR (Nujol; cm^{-1}): 1807 (ν(Fe−H)), 1224 (ν(HCS)), 984 ($\nu_{asym}(CS_2)$).

Reaction between *cis*-$Fe(dmpe)_2H_2$ (1) and CS_2 at 195 K. CS_2 (10−30 μL) was added at 195 K to an NMR tube containing a solution of *cis*-$Fe(dmpe)_2H_2$ (**1**) (25 mg, 0.07 mmol) in tetrahydrofuran-d_8 (0.5 mL) under nitrogen. According to NMR spectroscopy, the mixture contained starting material *cis*-$Fe(dmpe)_2H_2$ (**1**) and two products identified as *trans*-$Fe(dmpe)_2(SCHS)H$ (**4a**) and *cis*-$Fe(dmpe)_2(SCHS)H$ (**4b**). Complex **4b** was not stable above 240 K.

[OC-6-23]-Bis(1,2-bis(dimethylphosphino)ethane)(dithioformato)-hydridoiron(II), *cis*-$Fe(dmpe)_2(SCHS)H$ (4b). ^1H NMR (tetrahydrofuran-d_8, 220 K): δ −11.66 (m, 1H, Fe−*H*), 11.42 (s, 1H, SC*H*S). $^{31}P\{^1H\}$ NMR: δ 78.1 (m), 73.3 (m), 60.3 (m).

[OC-6-12]-Bis(1,2-bis(dimethylphosphino)ethane)bis-(dithioformato)iron(II), *trans*-$Fe(dmpe)_2(SCHS)_2$ (4c). CS_2 (45 μL, 0.7 mmol) was added at 300 K to an NMR tube containing a solution of *cis*-$Fe(dmpe)_2H_2$ (**1**) (25 mg, 0.07 mmol) under nitrogen in tetrahydrofuran-d_8 (0.5 mL). Dark purple crystals of **4c** precipitated, and the mixture was filtered. ^1H NMR (tetrahydrofuran-d_8, 300 K): δ 1.50 (s, 24H, PCH_3), 2.27 (br s, 8H, PCH_2), 11.06 (s, 2H, SC*H*S). $^{31}P\{^1H\}$ NMR: δ 66.2 (s). IR (Nujol; cm^{-1}): 1226 (ν(HCS)), 973 ($\nu_{asym}(CS_2)$).

[OC-6-32]-Bis(1,2-bis(dimethylphosphino)ethane)hydrido-(thioformato)iron(II), *trans*-$Fe(dmpe)_2(SCHO)H$ (5a). COS (1 atm) was added at 300 K to an NMR tube containing a degassed solution of *cis*-$Fe(dmpe)_2H_2$ (**1**) (30 mg, 0.084 mmol) in tetrahydrofuran-d_8 (0.5 mL). NMR spectroscopy indicated quantitative formation of **5a**. The solvent was removed, the residue extracted into benzene, and the extract was filtered. Removal of benzene and recrystallization from hexane gave **5a** as a yellow-orange crystalline solid in analytically pure form (25 mg, 71%). Mp: 183−185 °C dec. Anal. Calcd for $C_{13}H_{34}FeOP_4S$: C, 37.33; H, 8.14. Found: C, 37.1; H, 8.2. ^1H NMR (tetrahydrofuran-d_8, 300 K): δ −24.40 (p, J_{PH} = 51 Hz, 1H, Fe−*H*), 1.28 (s, 12H, PCH_3), 1.41 (s, 12H, PCH_3), 1.65 (br s, 4H, PCH_2), 2.21 (br s, 4H, PCH_2), 10.44 (s, 1H, SC*H*O). $^{31}P\{^1H\}$ NMR: δ 76.6 (s). $^{13}C\{^1H\}$ NMR: δ 16.8 (s, PCH_3), 24.9 (br s, PCH_3), 32.8 (p, J_{CP} = 14 Hz, PCH_2), 201.9 (s, SCHO). IR (Nujol; cm^{-1}): 1798 (ν(Fe−H)), 1632, 1548 (ν(CO)). Slow evaporation from hexane gave a single crystal of **5a** suitable for X-ray analysis.

Reaction between *cis*-$Fe(dmpe)_2H_2$ (1) and COS at 195 K. COS (5−6 atm) was added at 195 K to an NMR tube containing a degassed solution of *cis*-$Fe(dmpe)_2H_2$ (**1**) (25 mg, 0.07 mmol) in tetrahydrofuran-d_8 (0.5 mL). According to NMR spectroscopy, the mixture contained starting material *cis*-$Fe(dmpe)_2H_2$ (**1**) and three products identified as *trans*-$Fe(dmpe)_2(SCHO)H$ (**5a**) and two new isomeric $Fe(dmpe)_2(SCHO)H$ compounds **5b1** and **5b2**, which have not yet been fully characterized.

5b1. ^1H NMR (tetrahydrofuran-d_8, 240 K): δ −11.27 (m, 1H, Fe−*H*), 10.31 (s, 1H, SC*H*O). $^{31}P\{^1H\}$ NMR: δ 79.6 (m), 77.5 (dd, J_{PP} = 34 Hz, J_{PP} = 132 Hz), 72.1 (dd, J_{PP} = 24 Hz, J_{PP} = 133 Hz), 61.0 (m).

5b2. This compound was only stable below 220 K. ^1H NMR (tetrahydrofuran-d_8, 220 K): δ −9.44 (m, 1H, Fe−*H*), 9.65 (s, 1H, SC*H*O). $^{31}P\{^1H\}$ NMR: δ 83.3, 77.3, 66.3.

[OC-6-22]-Bis(1,2-bis(dimethylphosphino)ethane)bis(thioformato)-iron(II), *cis*-$Fe(dmpe)_2(SCHO)_2$ (5c). COS (5−6 atm) was added at 195 K to an NMR tube containing a degassed solution of *cis*-$Fe(dmpe)_2H_2$ (**1**) (30 mg, 0.084 mmol) in tetrahydrofuran-d_8 (0.5 mL). The sample was slowly warmed to 300 K, the solvent was removed, the residue was extracted into benzene, and the extract was filtered. Benzene was removed, and the residue was washed with ether to give **5c** as a red-purple solid in analytically pure form (28 mg, 70%). Mp: 175 °C dec. Anal. Calcd for $C_{14}H_{34}FeO_2P_4S_2$: C, 35.16; H, 7.12. Found: C, 35.0; H, 7.4. ^1H NMR (toluene-d_8, 300 K): δ 0.65 (d, J_{PH} = 5 Hz, 6H, PCH_3), 0.76 (br m, 2H, PCH_2), 1.04 (d, J_{PH} = 7 Hz, 6H, PCH_3), 1.16−1.45 (br m, 4H, PCH_2), 1.52 (s, 6H, PCH_3), 1.65 (br m, 2H, PCH_2), 1.71 (br s, 6H, PCH_3), 10.85 (s, 2H, SC*H*O). $^{31}P\{^1H\}$ NMR: δ 62.2 (t), 59.5 (t). $^{13}C\{^1H\}$ NMR: δ 13.4, 18.4, 19.8 (PCH_3), 28.7 (m, PCH_2), 33.4 (m, PCH_2), 200.5 (dt, SCHO). IR (Nujol; cm^{-1}): 1609, 1549 (ν(CO)).

[OC-6-12]-Bis(1,2-bis(dimethylphosphino)ethane)bis(thioformato)-iron(II), *trans*-$Fe(dmpe)_2(SCHO)_2$ (5d). COS (5−6 atm) was added at 300 K to an NMR tube containing a degassed solution of *trans*-$Fe(dmpe)_2(SCHO)H$ (**5a**) (prepared in situ from 25 mg (0.07 mmol) of *cis*-$Fe(dmpe)_2H_2$ (**1**)) in tetrahydrofuran-d_8 (0.5 mL). The solvent was removed, the residue was extracted into benzene, and the extract was filtered. Benzene was removed, and the residue was washed with ether to give **5d** as a red-purple solid (28 mg, 84%). ^1H NMR (tetrahydrofuran-d_8, 300 K): δ 1.43 (s, 24H, PCH_3), 2.38 (br s, 8H, PCH_2), 10.12 (s, 2H, SC*H*O). $^{31}P\{^1H\}$ NMR: δ 65.3 (s). $^{13}C\{^1H\}$ NMR: δ 16.3 (s, PCH_3), 31.8 (p, J_{CP} = 12 Hz, PCH_2), 200.9 (s, SCHO). IR (Nujol; cm^{-1}): 1609, 1551 (ν(CO)).

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[OC-6-34]-(Formato)hydrido(tris(2-(dimethylphosphino)ethyl)phosphine)iron(II), *cis*-Fe(PP$_3$)(OCHO)H (6a). CO_2 (1 atm) was added at 300 K to an NMR tube containing a degassed solution of *cis*-Fe(PP$_3$)H$_2$ (**2**) (20 mg, 0.058 mmol) in benzene-d_6 (0.5 mL). NMR spectroscopy indicated quantitative formation of **6a**. Removal of solvent and recrystallization from ether gave **6a** as an orange crystalline solid in analytically pure form (16 mg, 70%). Mp: 175 °C dec. Anal. Calcd for $C_{13}H_{32}FeO_2P_4$: C, 39.02; H, 8.06. Found: C, 39.7; H, 7.7. ^{1}H NMR (benzene-d_6, 300 K): δ −11.88 (tt, J_{PH} = 44, 68 Hz, Fe−*H*), 0.82−1.37 (P$_A$(C*H*$_2$C*H*$_2$P(CH$_3$)$_2$)$_3$), 1.29, 1.67 (2 × s, 2 × 6H, 2 × P$_T$(C*H*$_3$)), 1.46 (s, 6H, P$_E$(C*H*$_3$)$_2$), 9.23 (s, 1H, OC*H*O). ^{31}P{^{1}H} NMR: δ 179.2 (q, J = 18 Hz, 1P, P_A), 60.8 (t, J = 24 Hz, 2P, P_T), 56.8 (q, J = 18 Hz, 1P, P_E). ^{13}C{^{1}H} NMR: δ 19.7, 20.0 (d), 23.5 (m), 27.0 (m), 28.1 (m), 33.9 (dd), 34.5 (m) (P$_A$(*C*H$_2$*C*H$_2$P(*C*H$_3$)$_2$)$_3$), 169.9 (s, O*C*HO). IR (Nujol; cm^{-1}): 1797 (ν(Fe−H)), 1603 (ν_{asym}(CO$_2$)), 1320 (ν_{sym}(CO$_2$)).

[OC-6-33]-Bis(formato)(tris(2-(dimethylphosphino)ethyl)phosphine)iron(II), *cis*-Fe(PP$_3$)(OCHO)$_2$ (6b). CO_2 (5−6 atm) was added at 300 K to an NMR tube containing a degassed solution of *cis*-Fe(PP$_3$)H$_2$ (**2**) (10 mg, 0.029 mmol) in benzene-d_6 (0.5 mL). NMR spectroscopy indicated formation of **6b** as the dominant product. The product was only stable under a positive pressure of CO_2 and decomposed to an insoluble, uncharacterized product after 45 min. ^{1}H NMR (benzene-d_6, 300 K): δ 0.48−2.65 (m, P$_A$(C*H*$_2$C*H*$_2$P(C*H*$_3$)$_2$)$_3$), 8.60 (s, 1H, OC*H*O (trans to P$_E$)), 9.15 (s, 1H, OC*H*O (trans to P$_A$)). ^{31}P{^{1}H} NMR: δ 166.2 (apparent q, J = 28 Hz, 1P, P_A), 76.5 (dt, $J_{P_EP_T}$ = 48 Hz, $J_{P_EP_A}$ = 28 Hz, 1P, P_E), 50.1 (dd, $J_{P_TP_E}$ = 48 Hz, $J_{P_TP_A}$ = 28 Hz, 2P, P_T).

[OC-6-24]-(Dithioformato)hydrido(tris(2-(dimethylphosphino)ethyl)phosphine)iron(II), *cis*-Fe(PP$_3$)(SCHS)H (7a). CS_2 (1.5 μL, 0.025 mmol, 0.75 equiv) was added at 195 K to an NMR tube containing a solution of *cis*-Fe(PP$_3$)H$_2$ (**2**) (12 mg, 0.034 mmol) in toluene-d_8 (0.5 mL) under argon. NMR spectroscopy indicated the presence of starting material and **7a** in a ratio of 1:3. The resulting product in solution was warmed to 300 K. The addition of a slight excess of CS_2 (a further 1 μL) at 300 K allowed complete conversion of starting material to **7a** with subsequent conversion to an insoluble, uncharacterized product within 15 min. ^{1}H NMR (toluene-d_8, 300 K): δ −14.19 (m, 1H, Fe−*H*), 0.50−2.00 (m, 12H, P$_A$(C*H*$_2$C*H*$_2$P(CH$_3$)$_2$), 1.09, 2.00 (2 × s, 2 × 6H, 2 × P$_T$(C*H*$_3$)), 1.32 (s, 6H, P$_E$(C*H*$_3$)$_2$), 12.61 (s, 1H, SC*H*S). ^{31}P{^{1}H} NMR: δ 177.6 (q, J = 24 Hz, 1P, P_A), 62.7 (t, J = 24 Hz, 2P, P_T), 50.1 (q, J = 24 Hz, 1P, P_E). ^{13}C{^{1}H} NMR: δ 24.3 (m), 26.2 (br s), 27.4 (br s), 30.1, 35.3 (m), 36.4 (m), 38.2 (m) (P$_A$(*C*H$_2$*C*H$_2$P(*C*H$_3$)$_2$)$_3$), 237.5 (s, S*C*HS).

[OC-6-24]-Hydrido(thioformato)(tris(2-(dimethylphosphino)ethyl)phosphine)iron(II), *cis*-Fe(PP$_3$)(SCHO)H (8a). COS (1 atm) was added at 300 K to an NMR tube containing a degassed solution of *cis*-Fe(PP$_3$)H$_2$ (**2**) (20 mg, 0.058 mmol) in benzene (0.5 mL). The solvent and COS were removed in vacuo, and the stable solid was dissolved in benzene-d_6. NMR spectroscopy indicated quantitative formation of **8a**. The solvent was removed, and recrystallization from ether gave **8a** as a yellow crystalline solid (16 mg, 67%). ^{1}H NMR (benzene-d_6, 300 K): δ −14.12 (ddt, J_{P_TH} = 66 Hz, J_{P_AH} = 42 Hz, J_{P_EH} = 32 Hz, 1H, Fe−*H*), 0.97−1.35 (m, 12H, P$_A$(C*H*$_2$C*H*$_2$P(CH$_3$)$_2$), 1.22, 1.50 (2 × s, 2 × 6H, 2 × P$_T$(C*H*$_3$)), 1.41 (s, 6H, P$_E$(C*H*$_3$)$_2$), 11.48 (s, 1H, SC*H*O). ^{31}P{^{1}H} NMR: δ 181.1 (q, J = 28 Hz, 1P, P_A), 63.1 (dd, J = 24, 28 Hz, 2P, P_T), 61.9 (q, J = 24 Hz, 1P, P_E). ^{13}C{^{1}H} NMR: δ 19.0 (br s), 20.5 (d), 21.2 (br s), 25.2 (m), 27.0 (m), 35.2 (m), 35.8 (m) (P$_A$(*C*H$_2$*C*H$_2$P(*C*H$_3$)$_2$)$_3$), 202.3 (s, S*C*HO). IR (Nujol; cm^{-1}): 1808 (ν(Fe−H)), 1614, 1538 (ν(CO)).

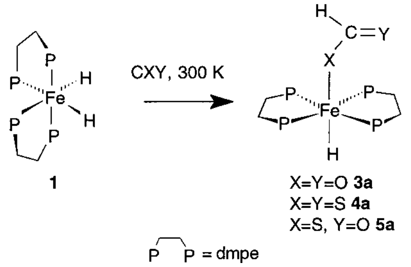
[OC-6-23]-Bis(thioformato)(tris(2-(dimethylphosphino)ethyl)phosphine)iron(II), *cis*-Fe(PP$_3$)(SCHO)$_2$ (8b). COS (5−6 atm) was added at 300 K to an NMR tube containing a degassed solution of **2** (12 mg, 0.034 mmol) in benzene-d_6 (0.5 mL). NMR spectroscopy indicated quantitative formation of **8b**. The solvent was removed, and recrystallization from benzene gave **8b** as an orange solid (5 mg, 30%). ^{1}H NMR (benzene-d_6, 300 K): δ 0.48−2.65 (m, 30H, P$_A$(C*H*$_2$C*H*$_2$P(C*H*$_3$)$_2$), 10.65 (s, 1H, SC*H*O (trans to P$_E$)), 11.17 (s, 1H, SC*H*O (trans to P$_A$)). ^{31}P{^{1}H} NMR: δ 178.7 (dt, $J_{P_TP_A}$ = $J_{P_EP_A}$ = 21 Hz, 1P, P_A), 72.4 (dt, $J_{P_EP_T}$ = 44 Hz, $J_{P_EP_A}$ = 24 Hz, 1P, P_E), 53.5 (dd, $J_{P_TP_E}$ = 44 Hz, $J_{P_TP_A}$ = 21 Hz, 2P, P_T). ^{13}C{^{1}H} NMR: δ 15.2 (m), 20.5 (d), 21.2 (br s), 27.0 (m), 31.9 (m), 33.6 (m), 36.0 (m) (P$_A$(*C*H$_2$*C*H$_2$P(*C*H$_3$)$_2$)$_3$), 202.9 (s, S*C*HO (trans to P$_A$)), 200.7 (s, S*C*HO (trans to P$_E$)).

Table 1. Crystallographic Data for *trans*-Fe(dmpe)$_2$(SCHO)H (**5a**)

empirical formula	$C_{13}H_{34}FeOP_4S$	temperature	−100 °C
fw	418.19	λ(Mo Kα)	0.710 73 Å
space group; *Z*	$P2_1/n$ (No. 14); 8	μ(Mo Kα)	1.128 cm^{-1}
lattice parameters	a = 14.1418(14) Å	ρ_{calcd}	1.336 g cm^{-3}
	b = 16.9976(17) Å	R1^a	0.0458
	c = 18.2308(18) Å	wR2^a	0.1118
	β = 108.337(2)°		
	V = 4159.7(7) Å^3		

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_c 2)^2]^{1/2}$ for all reflections; $w = 1/[\sigma^2(F_o^2) + (0.0508P)^2 + 1.8264P]$ where $P = (F_o^2 + 2F_c^2)/3$.

Scheme 1



X-ray Measurements for *trans*-Fe(dmpe)$_2$(SCHO)H (5a). Crystals of **5a** decomposed readily at room temperature. A yellow bladelike crystal was attached, with Exxon Paratone N, to a short length of fiber supported on a thin piece of copper wire inserted into a copper mounting pin. The crystal was quenched in a cold nitrogen gas stream upon mounting on a Bruker SMART 1000 diffractometer equipped with an Oxford Cryosystems Cryostream. Graphite-monochromated Mo Kα radiation was generated from a sealed tube. Cell constants were obtained from a least-squares refinement against 4436 reflections located in the range 5.28 < 2θ < 55.01°. Data were collected at 173(2) K with ω scans to 2θ = 56.68°. The intensities of 325 standard reflections recollected at the end of the experiment did not change significantly during the data collection. An empirical absorption correction determined with SADABS[16] was applied to the data. The data integration and reduction were undertaken with SAINT and XPREP,[17] and subsequent computations were carried out with the teXsan[18] graphical user interface. The structure was solved in the space group $P2_1/n$ (No. 14) by direct methods with SHELXS-97[19] and extended and refined with SHELXL-97.[20] The asymmetric unit was found to contain two crystallographically independent complex molecules. Anisotropic thermal parameters were refined for the non-hydrogen atoms of the structure model, and a riding-atom model was used for most of the hydrogen atoms. Peaks corresponding to anticipated hydride sites were located in late difference maps. Both hydrides were initially modeled with isotropic displacement parameters; however, a restraint was needed for the displacement parameter of H(Fe2). An abbreviated summary of the crystallographic data is given in Table 1.

Results and Discussion

Solutions of *cis*-Fe(dmpe)$_2$H$_2$ (**1**) in tetrahydrofuran-d_8 react with CO_2 (1 atm), CS_2 (2 equiv), and COS (1 atm) at 300 K to

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Table 2. Summary of ^1H, ^{31}P, and ^{13}C NMR and IR Data for Complexes **1**−**8b**

	NMR (δ)				IR (cm^{-1})	
	^1H			^{13}C		
compd	hydride	formate	^{31}P	C=X	ν(M−H)	$\nu(CX_2)$
cis-Fe(dmpe)$_2$H$_2$ **(1)**	−14.33		83.7, 74.7		1777	
cis-Fe(PP$_3$)H$_2$ **(2)**	−11.03		187.2, 68.7		1828, 1713	
trans-Fe(dmpe)$_2$(OCHO)H **(3a)**	−33.96	7.78	79.1	168.1	1805	$\nu_{as}(CO_2)$ 1602 $\nu_s(CO_2)$ 1328
trans-Fe(dmpe)$_2$(OCHO)$_2$ **(3b)**		6.46	69.9	170.5		$\nu_{as}(CO_2)$ 1607 $\nu_s(CO_2)$ 1322
cis-Fe(PP$_3$)(OCHO)H **(6a)**	−11.88	9.23	179.2, 60.8, 56.8	169.9	1797	$\nu_{as}(CO_2)$ 1603 $\nu_s(CO_2)$ 1321
cis-Fe(PP$_3$)(OCHO)$_2$ **(6b)**		9.15, 8.60	166.2, 76.5, 50.0			
trans-Fe(dmpe)$_2$(SCHO)H **(5a)**	−24.40	10.44	76.6	201.9	1798	ν(CO) 1632, 1548
cis-Fe(dmpe)$_2$(SCHO)$_2$ **(5c)**		10.43	63.6, 61.2	200.5		ν(CO) 1609, 1549
trans-Fe(dmpe)$_2$(SCHO)$_2$ **(5d)**		10.12	65.3	200.9		ν(CO) 1609, 1551
cis-Fe(PP$_3$)(SCHO)H **(8a)**	−14.12	11.48	181.1, 63.1, 61.9	202.3	1808	ν(CO) 1614, 1538
cis-Fe(PP$_3$)(SCHO)$_2$ **(8b)**		11.17, 10.65	178.7, 72.4, 53.5	202.9, 200.7		
trans-Fe(dmpe)$_2$(SCHS)H **(4a)**	−23.29	11.66	76.1	237.6	1807	$\nu_{as}(CS_2)$ 984
cis-Fe(dmpe)$_2$(SCHS)H **(4b)**	−11.64	11.48	77.8, 73.6, 60.1			
trans-Fe(dmpe)$_2$(SCHS)$_2$ **(4c)**		11.06	66.2			$\nu_{as}(CS_2)$ 973
cis-Fe(PP$_3$)(SCHS)H **(7a)**	−14.19	12.61	177.6, 62.7, 50.1	237.5		

give the insertion products *trans*-Fe(dmpe)$_2$(XCHY)H (X, Y = O, S) (Scheme 1). The $^{31}P\{^1H\}$ NMR spectra of **3a**, **4a**, and **5a** (Table 2) all exhibit a single singlet resonance, indicating a trans geometry around the iron center.

The ^1H NMR spectrum of *trans*-Fe(dmpe)$_2$(OCHO)H (**3a**) exhibits a high-field pentet at δ −33.96 for a hydride coupled to four ^{31}P nuclei ($^2J_{PH}$ = 49 Hz) and a singlet at δ 7.78 indicative of a formyl proton (such resonances characteristically appear between δ 7.47 and δ 9.32).[2,4,5,7−9,21,22] The $^{13}C\{^1H\}$ NMR spectrum shows a pentet at δ 168.1 ($^3J_{CP}$ = 95 Hz) for the carbonyl carbon (for metal formates, carbonyl resonances typically occur between δ 166.9 and δ 184.3).[2,4−10,21] The identification of an η^1-formate is confirmed by the appearance of two bands at 1602 and 1328 cm^{-1} in the IR spectrum. Other η^1-formates show $\nu_{asym}(CO_2)$ bands in the range 1603−1667 cm^{-1},[2,4,5,7,8,10,21,23,24] whereas η^2-formates generally show $\nu_{asym}(CO_2)$ bands between 1554 and 1585 cm^{-1}.[3,6,8,10,22]

The ^1H NMR spectrum of *trans*-Fe(dmpe)$_2$(SCHS)H (**4a**) displays a pentet resonance at δ −23.29 ($^2J_{PH}$ = 51 Hz), downfield from the corresponding hydride resonance of **3a**. The proton of the dithioformate ligand resonates at δ 11.66, comparable to the values for other metal dithioformates (δ 10.00−13.84).[21,22,25−28] In the $^{13}C\{^1H\}$ NMR spectrum, the C=S carbon resonates at δ 237.6 (Table 2), similar to the values for the previously reported metal dithioformates $[M(CO)_5(SCHS)]^-$ (M = Cr, W) (δ 237.4−239.3)[21] and upfield from the values for typical alkali metal dithiocarboxylates, which resonate in the range δ 250−277.[29] The IR spectrum shows a ν(HCS) band at 1224 cm^{-1}, comparable to the signals of other metal dithioformates (1215−1282 cm^{-1}),[12,25−28] and a $\nu_{asym}(CS_2)$ band at 984 cm^{-1}, in the region for η^1-dithioformates ($\nu_{asym}(CS_2)$ 980−1012 cm^{-1})[25] as opposed to η^2-dithioformates ($\nu_{asym}(CS_2)$ 900−960 cm^{-1}).[25−28]

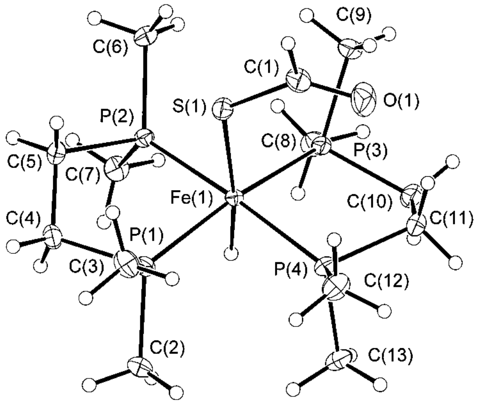

Figure 1. ORTEP diagram of *trans*-Fe(dmpe)$_2$(SCHO)H **(5a)** (25% ellipsoids).

The thioformate ligand in *trans*-Fe(dmpe)$_2$(SCHO)H (**5a**) can bind to the metal in an η^1 fashion through either the O or the S atom. The thioformyl proton (δ 10.44) and C=Y carbon (δ 201.9) in the ^1H and $^{13}C\{^1H\}$ NMR spectra, respectively, resonate midway between those of formate **3a** and dithioformate **4a** (Table 2), comparable to the case of other metal thioformates (δ 10.12−10.76 and δ 198.3−201.3, respectively).[8,21] The ^1H NMR spectrum also shows a metal hydride resonance at δ −24.40, similar to the resonance of **4a**, where the hydride is trans to an S atom. The IR spectrum displays two absorptions at 1632 and 1548 cm^{-1}, similar to the bands for copper(I) thioformates (1625−1635, 1570−1580 cm^{-1}).[8] Alkali metal thiocarboxylates show a single vibration between 1542 and 1510 cm^{-1}.[30] No C=S absorptions are observed, indicating that the sulfur is bound to the metal in **5a**.

Slow evaporation from hexane produces a single crystal of **5a** suitable for structure determination by X-ray crystallography (Figure 1). Selected bond lengths and angles are listed in Table 3. The unit cell contains two crystallographically independent complex molecules, both with octahedral iron(II) centers, coordinated by two bidentate dmpe ligands and an η^1 sulfur-

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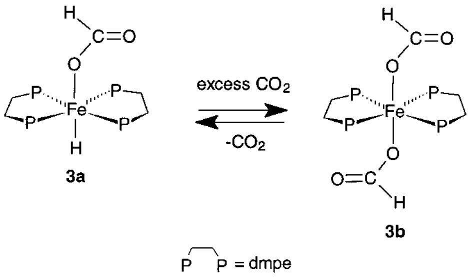
Table 3. Selected Bond Distances (Å) and Angles (deg) for *trans*-Fe(dmpe)$_2$(SCHO)H (**5a**)

Bond Distances			
Fe(1)−P(1)	2.2017(8)	Fe(1)−P(2)	2.1979(8)
Fe(1)−P(3)	2.1851(8)	Fe(1)−P(4)	2.1960(8)
Fe(2)−P(5)	2.1962(8)	Fe(2)−P(6)	2.1932(8)
Fe(2)−P(7)	2.1932(9)	Fe(2)−P(8)	2.1941(9)
S(1)−C(1)	1.710(3)	S(2)−C(14)	1.704(3)
O(1)−C(1)	1.217(4)	O(2)−C(14)	1.215(4)

Bond Angles			
P(2)−Fe(1)−P(1)	85.78(3)	P(4)−Fe(1)−P(1)	94.49(3)
P(3)−Fe(1)−P(4)	85.09(3)	P(3)−Fe(1)−P(2)	93.19(3)
P(6)−Fe(2)−P(7)	93.57(3)	P(7)−Fe(2)−P(8)	86.29(4)
P(8)−Fe(2)−P(5)	93.32(4)	P(6)−Fe(2)−P(5)	85.35(3)
P(1)−Fe(1)−S(1)	91.18(3)	P(2)−Fe(1)−S(1)	87.18(3)
P(3)−Fe(1)−S(1)	100.43(3)	P(4)−Fe(1)−S(1)	99.98(3)
P(5)−Fe(1)−S(2)	99.59(3)	P(6)−Fe(1)−S(2)	100.44(3)
P(7)−Fe(1)−S(2)	88.06(3)	P(8)−Fe(1)−S(2)	90.61(4)
O(1)−C(1)−S(1)	130.1(3)	O(2)−C(14)−S(2)	130.7(3)

Scheme 2



bound thioformate group trans to a hydride. The iron thioformate C═O bond distances (1.217(4), 1.215(4) Å) are slightly longer than the analogous distance in the chromium thioformate [Cr(CO)$_5$(SCHO)]$^-$ (1.206(6) Å),[21] and the iron atoms are respectively displaced from the least-squares plane P(1)−P(2)−P(3)−P(4) toward S(1) by 0.180 Å and from the least-squares plane P(5)−P(6)−P(7)−P(8) toward S(2) by 0.179 Å.

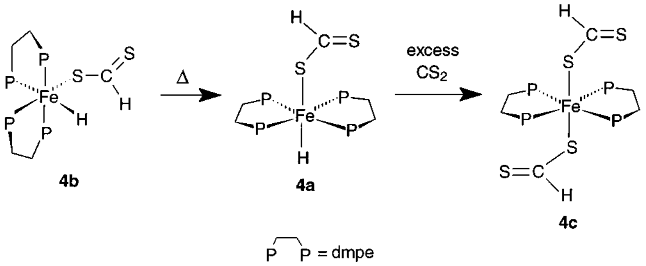
The thermodynamic product of the reaction contains an S-bound thioformate ligand, and this is consistent with previous reports of COS addition to iron hydrides.[8,21] The direction of addition is as expected from the preference of the relatively soft Fe(II) metal for the soft sulfur center in the ambident donor.

The addition of CO$_2$ (1 atm) to **1** at 195 K in tetrahydrofuran-*d*$_8$ produces *trans*-Fe(dmpe)$_2$(OCHO)H (**3a**) and unreacted **1**. Neither *cis*-Fe(dmpe)$_2$(OCHO)H (the expected intermediate in the formation of **3a**) nor *cis*-Fe(dmpe)$_2$(OCHO)$_2$ was observed in the ^{1}H and ^{31}P NMR spectra, as has been reported for the analogous ruthenium complex Ru(dmpe)$_2$(OCHO)H.[4] Warming the sample to 300 K results in complete conversion to **3a**. When CO$_2$ (5−6 atm) is added to **1** at 195 K, the bisinsertion product *trans*-Fe(dmpe)$_2$(OCHO)$_2$ (**3b**) is observed in the ^{1}H and ^{31}P NMR spectra and is formed almost exclusively when the sample is warmed to 300 K. When the sample is degassed, however, **3b** reversibly loses CO$_2$ to form **3a** (Scheme 2).

trans-Fe(dmpe)$_2$(OCHO)H (**3a**) is one of few metal hydrides to reversibly bind CO$_2$, and the loss of CO$_2$ from **3b** may provide insight into the mechanism of the final steps of the iron-catalyzed water gas shift reaction, where an iron formate is proposed to lose CO$_2$ to generate a metal hydride.[31]

The ^{31}P{^{1}H} NMR spectrum of **3b** displays a single resonance, indicating a trans geometry. No metal hydride resonances are observed in the ^{1}H NMR and IR spectra. The formate ligand displays a typical carbonyl resonance in the ^{13}C NMR spectrum, and the formyl proton (δ 6.46) is significantly upfield from the corresponding protons in **3a** and other metal formates[2,4−10,21,22] (Table 2).

Scheme 3



Green crystals of *trans*-Fe(dmpe)$_2$(OCHO)$_2$ (**3b**) suitable for a preliminary structure determination by X-ray crystallography were grown carefully in tetrahydrofuran-*d*$_8$ under 5−6 atm of CO$_2$ at 273 K. When the crystals were removed from a CO$_2$ atmosphere, they liberated CO$_2$ and lost their crystallinity. The crystal structure of **3b** was refined sufficiently well to confirm the presence of two bidentate dmpe ligands and two trans η^1-formate groups. The unit cell of **3b** contains two crystallographically independent molecules, both disordered about the iron(II) centers, where the iron(II)−formate (Fe−O) bond lengths (2.018 and 2.029 Å) are slightly longer than those of the iron(II) and iron(III) complexes Fe(η^1-C$_5$H$_5$)(CO)$_2$(OCHO), 1.957(2) Å,[24] and Fe(OEP)(OCHO), 1.910(4) Å (OEP = octaethylporphyrinate(2−)),[23] respectively.

The addition of CS$_2$ (2−8 equiv) to *cis*-Fe(dmpe)$_2$H$_2$ (**1**) at 195 K in tetrahydrofuran-*d*$_8$ yields mainly unreacted **1** in addition to *trans*-Fe(dmpe)$_2$(SCHS)H (**4a**). However, small amounts of the cis insertion product, *cis*-Fe(dmpe)$_2$(SCHS)H (**4b**) are observed at 220−240 K in the ^{1}H and ^{31}P NMR spectra. Warming the sample above this temperature results in the isomerization of **4b** to **4a**. The addition of 10 equiv of CS$_2$ to **1** forms the trans bisinsertion product *trans*-Fe(dmpe)$_2$(SCHS)$_2$ (**4c**) (Scheme 3), which decomposes in solution over a period of time to a mixture of products.

The ^{1}H NMR spectrum of *cis*-Fe(dmpe)$_2$(SCHS)H (**4b**) exhibits a hydride resonance at δ −11.64, which is consistent with a hydride trans to a phosphorus donor (Table 2). The ^{31}P{^{1}H} NMR spectrum displays three ^{31}P resonances at δ 78.1, 73.3, and 60.3, with those for the mutually trans phosphorus nuclei close to coincidence. The ^{1}H NMR spectrum of *trans*-Fe(dmpe)$_2$(SCHS)$_2$ (**4c**) exhibits the proton resonance of the dithioformate group at δ 11.06, upfield from those of **4a** and other metal dithioformates[21,22,25−28] (Table 2). The IR spectrum shows a ν_{asym}(CS$_2$) band at 973 cm^{-1}.

The addition of COS (1 atm) to *cis*-Fe(dmpe)$_2$H$_2$ (**1**) at 195 K in tetrahydrofuran-*d*$_8$ or toluene-*d*$_8$ results in a mixture of thioformate products. The complex *trans*-Fe(dmpe)$_2$(SCHO)H (**5a**) is easily identified by NMR spectroscopy. Two other products, **5b1** (not stable above 280 K) and **5b2** (not stable above 220 K), cannot be conclusively identified but are attributed to isomeric *cis*-Fe(dmpe)$_2$(SCHO)H complexes with different binding modes for the thioformate group. The possible binding modes for the thioformate group at the iron center, η^1-O, η^1-S, and η^2, could give rise to cis monoinsertion products **5b1** and **5b2**.

When an excess of COS (5−6 atm) is condensed into a sample of **1** at 195 K, resonances for four major iron(II) species are present in the ^{1}H and ^{31}P{^{1}H} NMR spectra at 220 K: **5a**,

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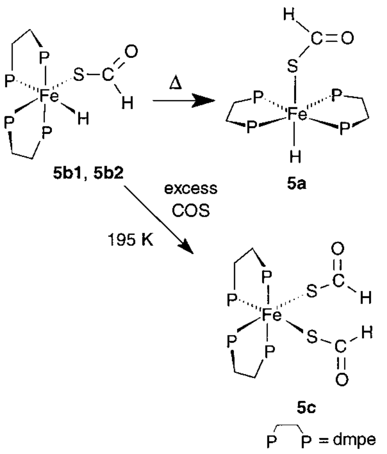
Scheme 4



5b1, **5b2**, and a cis bisinsertion product, *cis*-$Fe(dmpe)_2(SCHO)_2$ (**5c**) (Scheme 4). Complex **5b1** is stable at 280 K for several minutes before insertion of a second thioformate. Warming the sample to 300 K results in almost complete conversion to **5c** with small traces of *trans*-$Fe(dmpe)_2(SCHO)_2$ (**5d**). Complex **5c** is stable with removal of COS (Scheme 4) and constitutes the only thermally stable cis iron(II) formate complex in this series of iron(II)−dmpe complexes. Pure trans bisinsertion product **5d** is prepared independently by adding 5−6 atm of COS to **5a** and is stable with removal of COS (Scheme 4).

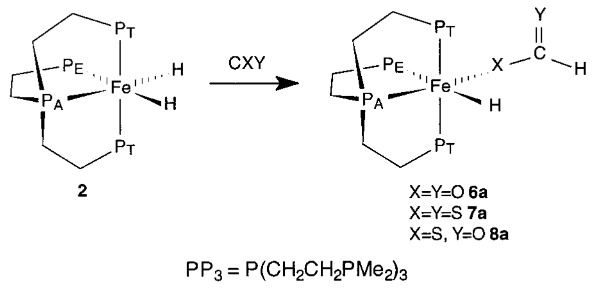
In the ^1H NMR spectrum at 220−240 K, complexes **5b1** and **5b2** display metal hydride resonances at δ −11.27 and −9.44 respectively, similar to the signals of other hydrides trans to phosphorus nuclei (Table 2). The hydride resonance for **5b2**, appearing at δ −9.44, is a broadened pentet, while the **5b1** hydride resonates at δ −11.27 as a multiplet. The $^{31}P\{^1H\}$ NMR spectrum reveals three phosphorus environments for **5b2** (similar to the cases of **4b** and *cis*-$Ru(dmpe)_2(OCHO)H^4$) and four phosphorus environments with the two trans phosphorus nuclei showing a coupling of 130 Hz for **5b1**. Both **5b1** and **5b2** exhibit thioformyl proton resonances in the ^1H NMR spectrum, with that of the **5b2** thioformyl proton (δ 9.65) upfield from those of other metal thioformates.[8,21]

cis-$Fe(dmpe)_2(SCHO)_2$ (**5c**) and *trans*-$Fe(dmpe)_2(SCHO)_2$ (**5d**) show no ^1H NMR metal hydride resonances and no IR metal−hydride absorptions. The thioformate ligands exhibit proton and carbonyl NMR shifts similar to those already observed in this work. The bis(thioformate) complex **5d** displays a singlet in its $^{31}P\{^1H\}$ NMR spectrum, while **5c** displays two apparent triplets (Table 2).

CO_2, COS, and CS_2 all react rapidly with the iron hydrides studied in this work. Although no quantitative kinetic analysis has been undertaken, CO_2 tends to react more rapidly than CS_2 or COS to form initial insertion products, which also have a stronger tendency to rearrange to more stable products.

With the exception of *cis*-$Fe(dmpe)_2(SCHO)_2$ (**5c**), the thermally stable product from each reaction of **1** with CO_2, CS_2, and COS possesses a trans geometry and no thermally stable *cis*-formato hydride complexes are observed. Examination of the reaction mixtures at low temperatures indicates that insertion products with cis stereochemistries are formed; however, these rearrange to trans products on warming. Iron complexes containing two bidentate phosphine ligands are well-known to be stereochemically labile, with cis and trans isomers being readily interconvertable under reaction conditions at or near room temperature. The relative stability of the $Fe(PP)_2X_2$ complexes can be rationalized by the fine balance between steric and electronic factors. The substituted tertiary phosphines are crowded at the Fe(II) center, and depending on the bulk of the substituents on P and the nature of the X ligands, $Fe(PP)_2X_2$ complexes have been characterized with either trans stereochemistry, e.g., $Fe(dmpe)_2Cl_2$,[32] $Fe(dmpe)_2HCl$,[33] $Fe(dmpe)_2(C{\equiv}CR)_2$,[34] and $Fe(dmpe)_2H(H)_2$,[35] or cis stereochemistry, e.g., $Fe(dmpe)_2H_2$[36] and $Fe(BPE5)_2Cl_2$ (BPE5 = 1,2-bis(phospholano)ethane),[37] or as an equilibrating mixture of the two, e.g., $Fe(dprpe)_2H_2$[38] and $Fe(dmpe)_2(SR)_2$.[39] A stable cis stereochemistry can be imposed on the metal system by replacement of the two dmpe ligands with the tetradentate phosphine ligand $P(CH_2CH_2PMe_2)_3$ (PP_3).

Scheme 5



Addition of CO_2 (1 atm) to a benzene-d_6 solution of the iron(II) dihydride *cis*-$Fe(PP_3)H_2$ (**2**) at 300 K results in an immediate reaction to form stable *cis*-$Fe(PP_3)(OCHO)H$ (**6a**) as the sole product (Scheme 5).

The $^{31}P\{^1H\}$ NMR spectrum of *cis*-$Fe(PP_3)(OCHO)H$ (**6a**) is typical of most octahedral complexes of the type *cis*-$Fe(PP_3)XY$,[15,40] showing a characteristic doublet of triplets for the apical, central phosphorus of the chelating PP_3 ligand (P_A) at δ 179.2, with signals at δ 60.81 and 56.8 for the axial terminal phosphorus resonances (P_T) and the equatorial terminal phosphorus resonance (P_E), respectively. The proton attached to the formate ligand resonates at δ 9.23 in the ^1H spectrum, downfield from the corresponding formyl protons in $Fe(dmpe)_2(OCHO)H$ and $Fe(dmpe)_2(OCHO)_2$, while the hydride appears at δ −11.88. The presence of the formate ligand was confirmed by a $^{13}C\{^1H\}$ NMR carbonyl resonance at δ 169.9 and IR absorptions at 1602 cm^{-1} ($\nu_{asym}(CO_2)$) and 1320 cm^{-1} ($\nu_{sym}(CO_2)$). 2D NOESY and COSY NMR techniques have been used to determine the geometry of complexes of the type *cis*-$Fe(PP_3)XH$,[15,40] and for all complexes of this type studied to date, the metal-bound hydride ligand has been located exclusively in a position cis to the apical phosphorus P_A. The downfield chemical shift, splitting pattern, and proton−phosphorus couplings confirm that **6a** also adopts this stereochemistry.

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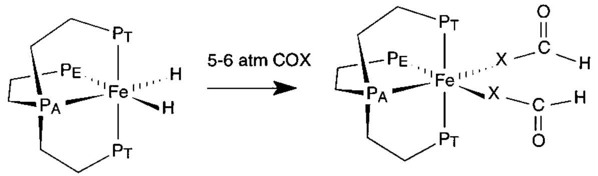
Scheme 6



2

X=O **6b**
X=S **8b**

$PP_3 = P(CH_2CH_2PMe_2)_3$

The addition of a large excess of CO_2 (5−6 atm) to a solution of **2** in benzene-d_6 at 300 K affords an unstable bis(formate) complex, *cis*-Fe(PP_3)$(OCHO)_2$ (**6b**) (Scheme 6), which reacts further with CO_2 to precipitate an uncharacterized product over the course of 45 min.

The $^{31}P\{^1H\}$ NMR spectrum of **6b** displays a doublet of triplets at δ 166.2 (P_A), a doublet of triplets at δ 76.5 (terminal phosphorus P_E), and a doublet of doublets at δ 50.1 (equivalent terminal phosphorus nuclei P_T). The relatively large upfield shift of P_E (relative to **6a**) is consistent with P_E being trans to a formate ligand. Two nonequivalent formyl protons resonate at δ 9.15 and 8.60 in the ^1H spectrum of **6b**, representing the protons from formate groups trans and cis to the apical phosphorus P_A, respectively.

When CS_2 (1 equiv) is added to a solution of *cis*-Fe(PP_3)H_2 (**2**) in toluene-d_8 at 300 K, a rapid reaction occurs, precipitating a dark red solid (which has not been further characterized) and leaving no identifiable products in solution. When CS_2 (0.75 equiv) is added at 195 K and the sample is slowly warmed to 300 K, however, two species are observable in solution: starting material **2** and *cis*-Fe(PP_3)(SCHS)H (**7a**), in a 1:3 ratio. The $^{31}P\{^1H\}$ NMR spectrum of **7a** exhibits a quartet at δ 177.6 (P_A), a triplet at δ 62.7 (P_T), and a quartet at δ 59.9 (P_E). The metal hydride of **7a** resonates as a multiplet at δ −14.19 and the dithioformyl proton resonates as a singlet at δ 12.61 in the ^1H NMR spectrum. The dithioformyl carbon resonates at δ 237.5 in the $^{13}C\{^1H\}$ NMR spectrum. Careful addition of more CS_2 to the mixture allows the quantitative formation of **7a** (Scheme 5), but this is followed by rapid decomposition to the insoluble solid observed previously. The bis(dithioformate) complex *cis*-Fe(PP_3)$(SCHS)_2$ is not observed.

When COS (1 atm) is added to a solution of *cis*-Fe(PP_3)H_2 (**2**) in benzene-d_6 at 300 K, the predominant product is the thioformato hydride complex *cis*-Fe(PP_3)(SCHO)H (**8a**) (Scheme 5), which is converted to the bis(thioformate) complex *cis*-Fe(PP_3)$(SCHO)_2$ (**8b**) in small amounts on standing. Removal of solvent and residual COS from a solution of **8a**, with subsequent reconstitution in benzene-d_6, affords **8a** as a stable compound. The $^{31}P\{^1H\}$ NMR spectrum of **8a** shows a doublet of triplets at δ 181.1 (P_A), a doublet of doublets at δ 63.1 (equivalent terminal phosphorus nuclei P_T), and a doublet of triplets at δ 61.9 (P_E). The thioformyl proton resonates at δ 11.48 in the ^1H NMR spectrum, while the hydride occurs as a doublet of doublets of triplets at δ −14.12. The P−H coupling constants again indicate that the hydride is cis to the apical phosphorus P_A. The thioformate is bound through its sulfur atom, as indicated by a characteristic carbonyl shift of δ 202.3 in the $^{13}C\{^1H\}$ NMR spectrum and two ν(CO) absorptions at 1614 and 1538 cm^{-1} in the IR spectrum.

The stable bis(thioformate) complex **8b** is formed quantitatively when *cis*-Fe(PP_3)H_2 (**2**) reacts with excess COS (5−6 atm) (Scheme 6). The apical phosphorus P_A resonates at δ 178.7, while the terminal phosphorus P_E occurs downfield at δ 72.4 (trans to a thioformate ligand). The equivalent phosphorus nuclei P_T resonate at δ 53.4 ppm. The two inequivalent thioformyl protons resonate at δ 11.17 and 10.65 for thioformate ligands trans to P_A and P_E, respectively. The $^{13}C\{^1H\}$ NMR spectrum displays resonances at δ 202.8 and 200.7 for carbonyl ^{13}C nuclei, again trans to P_A and P_E, respectively.

Conclusions

Iron dihydrides of the type FeP_4H_2 react rapidly with CO_2, COS, and CS_2, producing stable hydrido iron formates, thioformates, and dithioformates. In the case of *cis*-Fe$(dmpe)_2H_2$ (**1**), cis intermediates isomerize to the thermally stable trans insertion products between 195 and 280 K in the cases of CS_2 and COS, while the *cis*-formato hydride is not observed, allowing the reactivities of the three substrates to be qualified as COS < CS_2 < CO_2. The reaction with COS produces the isomer with sulfur bound to iron thermally, although there is evidence from low-temperature spectroscopy that a mixture of sulfur- and oxygen-bound species is formed initially and the oxygen-bound species isomerizes to the more stable sulfur-bound isomer. In the presence of excess CO_2, COS, and CS_2, bisinsertion products are produced; however, these are significantly less stable than the mono-insertion products. Complexes of the type $FeP_4(OCHO)_2$ readily lose CO_2 to revert to the hydridometal formates in the absence of high positive pressures of CO_2. This observation may mean that iron complexes of this type are suited to the catalysis of the retro water gas shift reaction or related reactions.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for *trans*-Fe$(dmpe)_2$(SCHO)H (**5a**). This material is available free of charge via the Internet at http://pubs.acs.org.

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