

Luminescent Iridium(I) Diethyldithiocarbamate Complexes: Synthesis, Structure, and Reactivity Including Stereoselective Hydrogen Oxidative Addition

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Abstract: A series of neutral Ir(I) complexes IrLL'(Et₂dtc) (L = L' = CO PPh₃, P(OPh)₃; L = CO, L' = PPh₃; L + L' = 1,2-bis(diphenylphosphino)ethane, 1,5-cyclooctadiene, 1,2-bis(di(pentafluorophenyl)phosphino)ethane; Et₂dtc = *N,N'*-diethyldithiocarbamate) has been synthesized and characterized by NMR, IR, and electronic spectroscopies. The complexes show spectra consistent with a four-coordinate structure. A distorted square planar coordination geometry is confirmed by a single crystal structure determination of Ir(CO)(PPh₃)(Et₂dtc) (**3**). Yellow-orange crystals of **3** (C₂₄H₂₅IrNOPS₂) are monoclinic, space group *P*2₁/*n* (no. 14), with *a* = 15.641(12) Å, *b* = 9.252(3) Å, *c* = 17.119(14) Å, β = 111.42(3)°, *V* = 2395.00 Å³, *Z* = 4, and final *R* = 0.029 (*R*_w = 0.031) for 3204 unique reflections. All of the complexes exhibit emission in the solid state and in frozen glass media at 77 K. Additionally, Ir(CO)(PPh₃)(Et₂dtc), Ir(dppe)(Et₂dtc), and Ir(P(OPh)₃)₂(Et₂dtc) display emission in methylene chloride solutions at room temperature. The bis triphenylphosphite complex, Ir(P(OPh)₃)₂(Et₂dtc), undergoes intramolecular C–H activation in benzene solution to form the ortho-metalated product Ir(P(OPh)₂(OC₆H₄))(H)(P(OPh)₃)(Et₂dtc). A benzene solution of Ir(CO)(PPh₃)(Et₂dtc) reacts readily with H₂, forming several different dihydride products having the formula IrH₂(CO)(PPh₃)(Et₂dtc), including an isomer with a kinetic preference for formation of 170:1 as determined using parahydrogen induced polarization (PHIP) at 300 K. A method is described for observing the ¹³C resonance of the carbonyl ligand in submilligram samples of IrH₂(PPh₃)(CO)(Et₂dtc) in under 2 min. The ligand exchange reactions of the two parahydrogen active isomers are also examined. PHIP is also observed in H₂ oxidative addition to Ir((C₆F₅)₂-PCH₂CH₂P(C₆F₅)₂)(Et₂dtc). Benzene solutions of Ir(CO)(PPh₃)(Et₂dtc) and Ir(dppe)(Et₂dtc) react with molecular oxygen to form the stable adducts Ir(O₂)(CO)(PPh₃)(Et₂dtc) and Ir(O₂)(dppe)(Et₂dtc), respectively, and both lose O₂ upon irradiation only. The complex Ir(CO)(PPh₃)(Et₂dtc) oxidatively adds CH₃I to form the trans addition product Ir(CH₃)(CO)(I)(PPh₃)(Et₂dtc).

Introduction

Interest in the chemistry of square planar platinum group element complexes is predicated on a number of factors. On the one hand, complexes of Rh(I), Ir(I), Pd(II), and Pt(II) have been found to be catalytically active for a variety of reactions including hydrogenation, hydroformylation, hydrosilylation, carbonylation, and olefin polymerization. In this context, the chemistry of Ir(I) systems has been extensively examined as modeling key steps in catalytic reactions, notably substrate activation by oxidative addition. The complex IrCl(CO)(PPh₃)₂ first reported by Vaska has been especially well investigated in this regard, and its reaction with molecular hydrogen is viewed as the quintessential example of a single step concerted oxidative addition reaction proceeding by a three-center transition state in which Ir–H bonds form concomitantly with H–H cleavage to yield a cis dihydride product.^{1,2} Factors influencing the course of this reaction have been probed extensively.^{3–8} In one

series of investigations from our laboratory, the cis di(phosphine) complexes IrX(CO)(dppe) where dppe = bis(diphenylphosphino)ethane were prepared, and the corresponding H₂ oxidative addition reaction examined with respect to the stereoselectivity of the reaction.^{9,10} In that study, it was determined that oxidative addition of H₂ and related Y–H substrates (Y = SiR₃, B(catecholate), halide) occur under kinetic control with a stereochemistry determined by ligand and substrate electronic effects.^{11,12} In the present paper, the range of substitution in the Ir(I) coordination sphere is probed further with a monoanionic chelating ligand that leads to a complex having properties very similar to Vaska's complex and a very high stereoselectivity for hydrogen addition.

A different facet of interest in square planar complexes lies in their excited state properties as manifested by luminescence. In the past ten years, there have been a large number of reports describing emissive d⁸ complexes of Rh(I), Ir(I), and Pt(II) with

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chelating diphosphine,^{13–18} diolefin,¹⁹ and diimine ligands.^{20–33} In 1983, our laboratory reported the synthesis and characterization of a series of luminescent square planar complexes of general formula $[\text{MLL}'(\text{mnt})]^-$ ($\text{M} = \text{Rh}, \text{Ir}; \text{L}, \text{L}' = \text{CO}, \text{PR}_3, \text{P}(\text{OR})_3$; $\text{mnt} = \text{maleonitriledithiolate}$).³⁴ These complexes exhibited highly structured emission and excitation spectra in the solid state and in frozen solution. From the similarity of the vibronic structure among Ir and Rh complexes, the shifts in emission maxima as a function of electron donating ability of L and L', and the observed lifetimes, the emissive transition was assigned as arising from a $^3(\text{d}-\pi^*_{\text{mnt}})$ excited state.

More recently, we have synthesized a series of Pt(diimine)-dithiolate complexes (diimine = bipyridine, *o*-phenanthroline, or alkylated derivative; dithiolate = mnt, toluenedithiolate (tdt) or 1-(ethoxycarbonyl)-1-cyanoethylene-2,2-dithiolate (ecda)).^{20–28,30,31} It was observed that the absorption spectra of all complexes exhibited solvatochromic behavior, while the emission spectra were dependent upon the dithiolate ligand. Specifically, emission bands from mnt complexes were structured, while tdt and ecda analogs possessed essentially featureless emission. Based on emission behavior as a function of temperature for these systems, mnt and tdt complexes were assigned as having a single emitting state, while the ecda complexes showed evidence of multiple emitting states. Different emitting states were thus assigned to Pt(II) diimine complexes of mnt and the other dithiolates with the mnt systems having a $^3(\text{Pt}(\text{d})/\text{S}(\text{p})-\pi^*_{\text{dithiolate}})$ emissive state, and the tdt and ecda complexes possessing a $^3(\text{Pt}(\text{d})/\text{S}(\text{p})-\pi^*_{\text{diimine}})$ lowest energy excited state. The difference in the emitting states was thought to arise from the difference in the π^* dithiolate energies for mnt, tdt, and ecda relative to the lowest unoccupied π^* levels of the diimine.

As a logical extension in the investigation of luminescent square planar complexes containing sulfur donor ligands, we have undertaken an investigation of neutral Ir(I) complexes having the uninegative chelating ligand *N,N'*-diethyldithiocarbamate (Et_2dtc). While the chemistry and electrochemistry of dithiocarbamates of Rh(I) and Rh(III) have been studied extensively,^{35–46} there are relatively few Ir(III) dithiocarbamate complexes that have been described and virtually no Ir(I) systems.^{47,48} In the present study, we describe a new series of square planar Ir(I) complexes having the general formula $\text{Ir}(\text{L})(\text{L}')(\text{Et}_2\text{dtc})$ ($\text{L} = \text{L}' = \text{CO}, \text{P}(\text{O}^i\text{Pr})_3, \text{PPh}_3$; $\text{L} + \text{L}' = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}, 1,2\text{-bis}(\text{di}(\text{pentafluorophenyl})\text{phosphino})\text{ethane}$; $\text{L} = \text{CO}, \text{L}' = \text{PPh}_3$). The synthesis and characterization of these complexes are reported as well as the single crystal X-ray structure determination of $\text{Ir}(\text{CO})(\text{PPh}_3)(\text{Et}_2\text{dtc})$. All of the complexes are luminescent in rigid media at 77 K, and several are found to emit in fluid solution at ambient temperature, representing the first time this has been seen for four-coordinate Ir(I) systems. Additionally, in connection with our interest in Ir(I) complexes for bond activation and catalysis, we have investigated the reactivity of some of these compounds with H_2 , O_2 , and methyl iodide. With regard to the first of these, we have employed parahydrogen induced polarization (PHIP) to probe the kinetic selectivity of oxidative addition and monitor the mechanism of interconversion between product isomers. PHIP is a sensitive and definitive method for determining pairwise hydrogen addition reactions and has recently been used in conjunction with 2-D HMQC experiments to assign structures and dynamics of metal hydrides.

Experimental Section

Materials and Methods. Reactions and sample preparations were conducted in a nitrogen filled glovebox or under the appropriate gas using a high vacuum line or Schlenk line. All solvents were reagent grade or better and were dried and degassed by accepted methods.⁴⁹ Hydrogen (99.99%, Air Products) and carbon monoxide (99.3%, Air Products) were used as received. The following compounds were used as received: 1,2-bis(diphenylphosphino)ethane (dppe), triphenylphosphine (PPh_3) (Aldrich), triphenylphosphite ($\text{P}(\text{O}^i\text{Pr})_3$) (Strem), methyl iodide (Aldrich), 1,2-bis(di(pentafluorophenyl)phosphino)ethane (Strem), sodium *N,N'*-diethyldithiocarbamate trihydrate ($\text{NaEt}_2\text{dtc}\cdot 3\text{H}_2\text{O}$) (Eastman). The EPA mixed solvent used for some of the emission measurements was prepared from five parts diethyl ether (Baker Phorex), five parts isopentane (Aldrich spectrophotometric grade), and

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two parts ethanol (Baker Photrex). Elemental analyses were performed by Desert Analytics Laboratory, Tucson, AZ.

Ir(COD)(Et₂dtc), 1. [Ir(COD)Cl]₂ (0.500 g, 0.744 mmol) and NaEt₂·3H₂O (0.336 g, 1.490 mmol) were dissolved in 50 mL of 1:1 (v/v) CH₂Cl₂–acetone, and the solution was stirred for 2 h. Filtration of NaCl through a 5 cm MgSO₄/SiO₂ column resulted in a yellow-orange solution which was concentrated under vacuum to about 10 mL. The solution was set aside at –20 °C for 3 h. The yellow-orange crystalline precipitate was collected by filtration and washed with cold hexane to give 0.560 g (84%) of Ir(COD)(Et₂dtc). Anal. Calcd for IrC₁₃H₂₂NS₂: C, 34.74; H, 4.94. Found: C, 34.82; H, 4.94.

Ir(CO)₂(Et₂dtc), 2. A solution of Ir(COD)(Et₂dtc) (0.073 g, 0.164 mmol) in 10 mL of CH₂Cl₂ was stirred for 10 min under a slow flow of CO. The red-orange solution was concentrated under vacuum to ca. 2 mL, and addition of 10 mL of degassed hexane afforded precipitation of a deep green-purple powder which was subsequently collected by filtration and washed with hexane to give 0.057 g (88%) of Ir(CO)₂(Et₂dtc). Anal. Calcd for IrC₇H₁₀NO₂S₂: C, 21.16; H, 2.54. Found: C, 21.39; H, 2.56.

Ir(CO)(PPh₃)(Et₂dtc), 3. A solution of Ir(COD)(Et₂dtc) (0.090 g, 0.203 mmol) in 30 mL of methylene chloride was stirred for 10 min under a slow flow of CO. To this red-orange solution was added 0.058 g (0.222 mmol) of PPh₃. The solution turned yellow, while gas evolution was observed. Upon concentration and addition of hexanes, a yellow crystalline precipitate formed. The solid was collected by filtration and washed with hexanes to give 0.100 g (78%) of Ir(CO)(PPh₃)(Et₂dtc). *m/z*: 731 M⁺. Anal. Calcd for IrC₂₄H₂₅NOPS₂: C, 45.64; H, 3.86. Found: C, 45.64; H, 3.99.

Ir(PPh₃)₂(Et₂dtc), 4. To a solution of Ir(COD)(Et₂dtc) (0.060 g, 0.135 mmol) in 30 mL of acetone was added 0.077 g of PPh₃ (0.294 mmol). The resultant red-orange solution was stirred for 1 h at room temperature and concentrated to 5 mL under vacuum. Upon addition of ether (10 mL), a powdery red precipitate formed that was collected by filtration and washed with ether to give 0.102 g (87%) of Ir(PPh₃)₂(Et₂dtc). Anal. Calcd for IrC₄₁H₄₀NP₂S₂: C, 56.80; H, 4.77. Found: C, 56.79; H, 4.66.

Ir(P(OPh)₃)₂(Et₂dtc), 5. To a solution of Ir(COD)(Et₂dtc) (0.100 g, 0.225 mmol) in 20 mL of CH₂Cl₂ was added 130 μL of P(OPh)₃ (0.153 g, 0.496 mmol). The resultant pale yellow solution was stirred for 20 min at room temperature and concentrated to 5 mL under vacuum. Upon addition of ether (10 mL), a yellow precipitate formed that was collected by filtration and washed with ether to give 0.168 g (78%) of Ir(P(OPh)₃)₂(Et₂dtc). Anal. Calcd for IrC₄₁H₄₀NP₂O₆S₂: C, 51.19; H, 4.19. Found: C, 50.98; H, 4.04.

Ir(dppe)(Et₂dtc), 6. To a solution of Ir(COD)(Et₂dtc) (0.100 g, 0.225 mmol) in 20 mL of acetone was added dppe (0.099 g, 0.247 mmol). The resultant orange solution was stirred for 1 h at room temperature and concentrated to 5 mL under vacuum. Upon addition of 10 mL of hexane, an orange powdery precipitate formed that was collected by filtration and washed with hexane to give 0.125 g (78%) of Ir(dppe)(Et₂dtc). *m/z*: 739 M⁺.

Ir(dpfp)(Et₂dtc), 7. To a solution of Ir(COD)(Et₂dtc) (0.075 g, 0.168 mmol) in 20 mL of acetone, dpfp (0.130 g, 0.172 mmol) was added. The resultant yellow-orange solution was stirred for 1 h at room temperature and concentrated under vacuum. Upon addition of 10 mL of hexane, a powdery yellow-orange precipitate formed that was collected by filtration and washed with ether to give 0.160 g (85%) of Ir(dpfp)(Et₂dtc).

Ir(P(OPh)₂(OC₆H₄))(H)(P(OPh)₃)(Et₂dtc), 8. A benzene-*d*₆ solution of complex **5** was allowed to stand under nitrogen for several hours. NMR resonances characteristic for complex **5** were quantitatively replaced by those of **8**.

IrH₂(CO)(PPh₃)₂(Et₂dtc), 9a-c. Hydrogen gas was admitted to a pressure of 2 atm to a resealable NMR tube containing a frozen solution of Ir(CO)(PPh₃)₂(Et₂dtc) in benzene-*d*₆. After warming the sample to 342 K in the probe and waiting for a total of 20 min, the ¹H NMR spectrum was recorded. This spectrum showed the presence of **9a**. After 20 h at room temperature, the ¹H NMR spectrum revealed the presence of the different isomers **9a-c**. For the PHIP experiments, hydrogen enriched in the para spin state was prepared by cooling H₂

to 77 K over a paramagnetic catalyst and then transferred to the resealable NMR tube.

IrH₂(PPh₃)₂(Et₂dtc), 10a,b. Hydrogen gas was admitted to a pressure of 2 atm to a resealable NMR tube containing a frozen solution of Ir(PPh₃)₂(Et₂dtc) in toluene-*d*₈. After warming the sample to 300 K in the probe, a ¹H NMR spectrum revealed the presence of **10a**. After 15 min at 300 K, **10b** was formed.

IrH₂(dpfp)(Et₂dtc), 11. Hydrogen gas enriched in the para spin state was admitted up to a pressure of 3 atm to a resealable NMR tube containing a frozen solution of Ir(dpfp)(Et₂dtc) in benzene-*d*₆. After warming the sample to 342 K in the probe, the ¹H NMR spectrum was recorded. This spectrum showed the presence of **11** as the sole hydride containing product.

Ir(CO)(O₂)(PPh₃)(Et₂dtc), 12. Molecular oxygen was bubbled through a yellow methylene chloride solution of **3** (0.075 g; 0.083 mmol) for ca. 10 min and then stirred an additional 1 h under an atm of O₂. Solution reduction to 2 mL followed by the addition of 35 mL of deaerated pentane yielded 0.056 g (71%) of **12** as a bright yellow powder.

Ir(O₂)(dppe)(Et₂dtc), 13. Molecular oxygen was bubbled through a yellow-orange methylene chloride solution of **6** (0.075 g; 0.083 mmol) for ca. 10 min and then stirred an additional 1 h under an atm of O₂. Solution reduction to 2 mL followed by the addition of 35 mL of deaerated pentane yielded 0.079 g (73%) of a yellow solid.

Ir(CH₃)(CO)(I)(PPh₃)(Et₂dtc), 14. To a 20 mL acetone solution of Ir(CO)(PPh₃)₂(Et₂dtc) (0.150 g, 0.237 mmol) was added 74 μL of CH₃I (0.168 g, 1.189 mmol). The yellow-orange solution was stirred for about 30 min. Upon concentration and addition of isopropyl alcohol, a yellow-tan powder precipitate was collected by filtration and washed with ether to give 0.162 g (88%) of Ir(CH₃)(CO)(I)(PPh₃)(Et₂dtc).

Spectroscopic Characterization. Most NMR samples were prepared using resealable NMR tubes fitted with J Young Teflon valves (Brunfeldt) and high vacuum line adapters. Otherwise, samples were placed in NMR tubes with high vacuum line adapters and flame sealed after solvent transfer. ¹H NMR spectra were recorded using either a Bruker AMX-400 or a Bruker AMX-500 spectrometer at 400.13 or 500.13 MHz, respectively, and ³¹P{¹H} NMR spectra were recorded using either a Bruker AMX-400 or a Bruker AMX-500 spectrometer at 161.98 or 202.404 MHz, respectively. ¹³C NMR spectra were recorded using a Bruker AMX-500 spectrometer at 125.1 MHz. ¹H NMR chemical shifts are reported in ppm downfield of tetramethylsilane but measured from residual ¹H signal in the deuterated solvents. ³¹P{¹H} NMR spectra are reported in ppm downfield of an external 85% solution of phosphoric acid. Infrared spectra were recorded from KBr pellet samples using a Mattson Galaxy 6020 FT IR spectrometer. Absorption spectra were recorded on a Hitachi U-2000 UV–visible spectrophotometer. Room temperature and low temperature emission measurements were performed on a Spex Fluorolog fluorescence spectrophotometer using a quartz dewar. Room temperature emission spectra were recorded in methylene chloride or butyronitrile. Low temperature emission and excitation spectra were recorded in EPA and butyronitrile glasses or in a KBr matrix. Mass spectra were collected using electron impact ionization on a VG autospectrometer.

Electrochemical Characterization. Electrochemical measurements were made at (20 ± 1) °C in degassed acetonitrile using a Princeton Applied Research (PAR) 173 potentiostat with a 179 and 175 sweep generator and a Houston 200 xy recorder. Cyclic voltammograms were measured using a single-compartment three electrode cell containing a glassy-carbon working electrode, a platinum wire auxiliary electrode, and a Ag wire quasi-reference electrode. Tetrabutylammonium hexafluorophosphate (TBAPF₆, 0.1 M) was used as the supporting electrolyte. Solutions were prepared in a nitrogen filled glovebox, and a continuous stream of nitrogen was passed over the solution while measurements were being performed. All oxidation and reduction waves are reported vs NHE based on using the ferrocene/ferrocenium couple (0.400 V) as an internal standard.

Crystal Structure Determination of Ir(CO)(PPh₃)(Et₂dtc), 3. A crystal suitable for X-ray diffraction was grown by slow diffusion of diethyl ether to a saturated acetone solution of the complex at –30 °C. The crystals were found to be moderately oxygen sensitive. A yellow-orange prism (dimension 0.30 mm × 0.26 mm × 0.24 mm) was mounted on a glass fiber using epoxy. The goniometer head was

Table 1. Crystallographic Data for Ir(CO)(PPh₃)(Et₂dtc), **3**

chemical formula	IrC ₂₄ H ₂₅ NOPS ₂
formula weight	626.8
crystal system	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i> (no. 14)
<i>Z</i>	4
<i>a</i> , Å	15.641(11)
<i>b</i> , Å	9.252(3)
<i>c</i> , Å	17.119(14)
β , deg	111.42(3)
<i>V</i> , Å ³	2395.0
ρ_{calc} , g/cm ³	1.749
<i>R</i> (<i>F</i> _o)	0.029
<i>R</i> _w (<i>F</i> _o)	0.031
GOF	1.045

Table 2. Selected Intramolecular Bond Distances^a and Bond Angles^b for Ir(CO)(PPh₃)(Et₂dtc), **3**

atoms	distance	atoms	angle
IR-S1	2.372(3)	S1-IR-S2	73.95(9)
IR-S2	2.384(3)	S1-IR-P1	173.54(9)
IR-P1	2.252(3)	S1-IR-C6	97.0(3)
IR-C6	1.79(1)	S2-IR-P1	99.59(9)
S1-C1	1.70(1)	S2-IR-C6	170.9(3)
S2-C1	1.75(1)	P1-IR-C6	89.5(3)
P1-C7	1.831(9)	IR-S1-C1	87.8(3)
P1-C13	1.83(1)	IR-S2-C1	86.3(3)
P1-C19	1.831(8)	C1-N1-C2	124.4(8)
O1-C6	1.17(1)	C1-N1-C4	119.5(8)
N1-C1	1.30(1)	C2-N1-C4	116.1(7)
N1-C2	1.46(1)	S1-C1-S2	111.9(5)
N1-C4	1.50(1)	S1-C1-N1	125.5(7)
C2-C3	1.52(1)	S2-C1-N1	122.6(7)
C4-C5	1.48(1)	IR-C6-O1	178(1)

^a Distances are in Å. ^b Angles are in deg. Estimated standard deviations in the least significant figure are given in parentheses.

mounted on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo K α radiation operating in the $\omega/2\theta$ scan mode. The crystal was found to be monoclinic, space group *P*2₁/*n*, with cell dimensions *a* = 15.641(12) Å, *b* = 9.252(3) Å, *c* = 17.119(14) Å, β = 111.42(3)°. Heavy atom methods were employed to locate the iridium atom. The remaining non-hydrogen atoms were located using cycles of difference Fourier maps and least square refinements. An empirical absorption correction using the program DIFABS was applied.⁵⁰ In the last refinement all non-hydrogen atoms were described with anisotropic thermal parameters. Hydrogen atoms were placed at calculated positions around the diethyldithiocarbamate ligand and around the phenyl rings. Neutral atom scattering factors were taken from Cromer and Waber.⁵¹ Anomalous dispersion effects were included in *F*_{calc}; the values $\Delta f'$ and $\Delta f''$ were those of Cromer.⁵² All calculations were performed using TEXSAN software.⁵³ Tables of abbreviated crystallographic data and selected bond lengths and angles are presented in Tables 1 and 2, respectively. The Supporting Information contains full crystallographic data, positional parameters for all atoms, final anisotropic thermal parameters, and complete tabulations of bond distances and angles. (See paragraph regarding Supporting Information at the end of paper.)

Results and Discussion

Synthesis and Characterization of Complexes. The complex Ir(COD)(Et₂dtc) (**1**) is prepared by reacting [Ir(μ -Cl)(COD)]₂ with the Na⁺ salt of *N,N'*-diethyldithiocarbamate in acetone/dichloromethane according to eq 1. All of the other

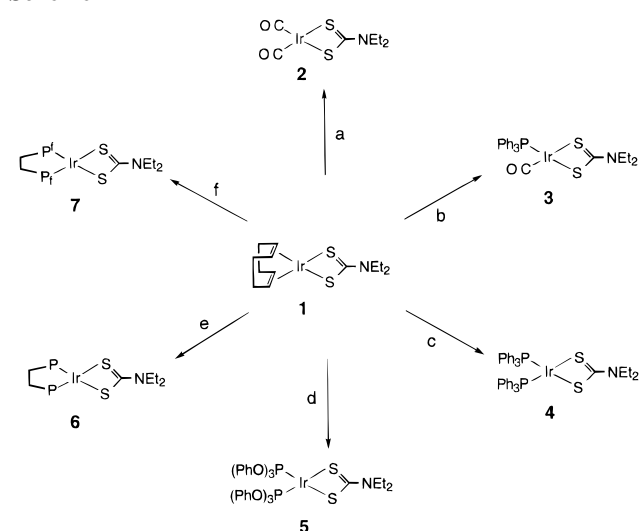
(50) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, A29, 158–166.

(51) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, p Table 2.2A.

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Scheme 1^a



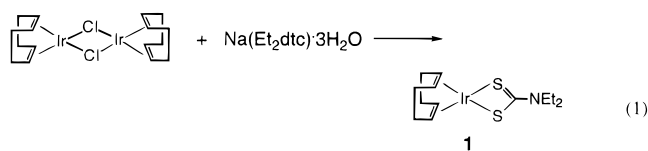
^a Conditions: (a) CO, CH₂Cl₂; (b) CO, 1.1 equiv of PPh₃, acetone; (c) 2.1 equiv of PPh₃, acetone; (d) 2.1 equiv of P(OPh)₃, CH₂Cl₂; (e) 1.1 equiv of dppe (dppe = 1,2-bis(diphenylphosphino)ethane), acetone; (f) 1.1 equiv of dpfp (dpfp = 1,2-bis(di(pentafluorophenyl)phosphino)ethane), acetone.

Table 3. Selected Infrared Spectral Data for Ir(L)(L')(Et₂dtc) Complexes^a

complex	ν_{CO}	$\nu_{\text{C-N}}$	$\nu_{\text{O-O}}$
1 Ir(COD)(Et ₂ dtc)		1514	
2 Ir(CO) ₂ (Et ₂ dtc)	2037, 1972	1521	
3 Ir(CO)(PPh ₃)(Et ₂ dtc)	1958	1525	
4 Ir(PPh ₃) ₂ (Et ₂ dtc)		1499	
5 Ir(P(OPh) ₃) ₂ (Et ₂ dtc)		1489	
6 Ir(dppe)(Et ₂ dtc)		1507	
7 Ir(dpfp)(Et ₂ dtc)		1518	
12 Ir(O ₂)(CO)(PPh ₃)(Et ₂ dtc)	1994	1517	843
13 Ir(O ₂)(dppe)(Et ₂ dtc)		1520	818
14 Ir(CH ₃)(CO)(I)(PPh ₃)(Et ₂ dtc)	2025	1515	

^a All spectra obtained from KBr pellets with bands given in wavenumbers (cm⁻¹).

new Ir(I) diethyldithiocarbamate complexes investigated in the present



work are shown in Scheme 1. All of the complexes are obtained in high yield as analytically pure solids and are characterized by IR and ¹H and ³¹P NMR spectroscopic data as presented in Tables 3 and 4, respectively.

A common feature in the infrared spectra of all of the complexes is a stretch around 1500–1520 cm⁻¹ corresponding to a ν_{CN} of the Et₂dtc ligand, while a dominant feature of all of the ¹H NMR spectra are the resonances corresponding to the ethyl protons of the Et₂dtc ligand. For complex **1**, the coordinated COD ligand is readily identified by the resonances arising from the two sets of methylene protons and the vinylic protons of bound diolefin. Substitution of COD proceeds readily under CO leading to complex **2** which exhibits two ν_{CO} at 2037 and 1972 cm⁻¹ consistent with a cis dicarbonyl arrangement about a four-coordinate Ir(I) center.^{54,55} Complex **2** is orange

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Table 4. ^1H and ^{31}P NMR Spectral Data for $\text{Ir}(\text{L})(\text{L}')(\text{Et}_2\text{dtc})$ Complexes^a

complex	^1H NMR ^b		$^{31}\text{P}\{^1\text{H}\}$ NMR ^b
	Et_2dtc	others ligands	
1 $\text{Ir}(\text{COD})(\text{Et}_2\text{dtc})$	0.67 t (7.2); 2.99 q (7.2)	1.46 m; 2.21 m; 4.32 m	
2 $\text{Ir}(\text{CO})_2(\text{Et}_2\text{dtc})$	0.48 t (7.2); 2.71 q (7.2)		
3 $\text{Ir}(\text{CO})(\text{PPh}_3)(\text{Et}_2\text{dtc})$	0.52 t (7.2); 0.67 t (7.2); 2.84 q (7.2); 3.01 q (7.2)	7.02 m; 7.88 m	21.61 s
4 $\text{Ir}(\text{PPh}_3)_2(\text{Et}_2\text{dtc})$	0.60 t (7.2); 2.98 q (7.2)	6.93 m; 7.91 m	23.40 s
5 $\text{Ir}(\text{P}(\text{OPh})_3)_2(\text{Et}_2\text{dtc})$	0.42 t (7.2); 2.74 q (7.2)	6.86 m; 7.04 m; 7.56 m	93.81 s
6 $\text{Ir}(\text{dppe})(\text{Et}_2\text{dtc})$	0.74 t (7.2); 3.15 q (7.2)	1.88 m; 7.04 m; 8.00 m	45.98 s
7 $\text{Ir}(\text{dpfpe})(\text{Et}_2\text{dtc})$	0.56 t (7.2); 2.95 q (7.2)	2.31 m	10.74 s
8 $\text{Ir}(\text{P}(\text{OPh})_2(\text{OC}_6\text{H}_4))(\text{H})(\text{P}(\text{OPh})_3)(\text{Et}_2\text{dtc})$	0.59 t (7.2); 0.84 t (7.2); 2.78 m; 3.01 m	-16.02 dd (17.1; 24.9); 6.70-8.40 m	88.60 d (21.8); 112.40 d (21.8)
9a $\text{IrH}_2(\text{CO})(\text{PPh}_3)(\text{Et}_2\text{dtc})$	3.12 m; 0.75 t (7.2); 0.72 t (7.2)	7.73 m; 7.04 m; -6.11 dd (20.1, 3.1); -15.70 dd (19.2, 3.1)	15.56 s
9b $\text{IrH}_2(\text{CO})(\text{PPh}_3)(\text{Et}_2\text{dtc})$	0.538 t (7.1); 0.55 t (7.1)	-7.74 dd (166.5, 3.9); -14.76 dd (10.9, 4.4)	4.59 s
9c $\text{IrH}_2(\text{CO})(\text{PPh}_3)(\text{Et}_2\text{dtc})$	0.63 t (7.1)	-16.52 d (18.6)	13.03 s
10a $\text{IrH}_2(\text{PPh}_3)_2(\text{Et}_2\text{dtc})$	0.70 t (7.0); 3.03 q (7.0)	7.75 m; 6.95 m; -9.21 ddd (157.6, 22.6, 3.7); -17.35 ddd (18.0, 14.0, 3.7)	9.61 d (6.9); -18.3 d (6.9)
10b $\text{IrH}_2(\text{PPh}_3)_2(\text{Et}_2\text{dtc})$	0.65 t (7.0); 2.81 q (7.0)	8.01 m; 7.07 m; -18.44 t (16.8)	17.8 s
11 $\text{IrH}_2(\text{dpfpe})(\text{Et}_2\text{dtc})$	0.57 t (7.1); 0.74 t (7.1); 2.64 spt (7.14); 2.96 m; 3.11 m	2.18 m; 2.49 m; 3.11 m; 3.25 m; -5.92 m; -16.89 m	7.86 m; 0.34 m
12 $\text{Ir}(\text{CO})(\text{O}_2)(\text{PPh}_3)(\text{Et}_2\text{dtc})$	0.55 t (7.2); 0.56 t (7.2); 2.68-3.02 m	6.99 m; 7.74 m	2.40 s
13 $\text{Ir}(\text{O}_2)(\text{dppe})(\text{Et}_2\text{dtc})$	0.33 t; 0.48 t; 2.84 m; 2.61 m; 2.37 m	2.13 m; 8.17-6.92 m	32.44 s; 14.00 s
14 $\text{Ir}(\text{CH}_3)(\text{CO})(\text{I})(\text{PPh}_3)(\text{Et}_2\text{dtc})$	0.62 t (7.2); 0.69 t (7.2); 2.88 m	1.65 d (4.1); 7.02 m; 7.87 m	-1.17 s

^a 400 MHz, C_6D_6 solutions. ^b 500 MHz, $\text{C}_6\text{D}_5\text{CD}_3$. ^c Chemical shift values are reported in ppm, coupling constant in parentheses are in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; spt, septet.

in fluid solution and dark purple as a solid. The dark purple color is indicative of stacking in the solid state as has been observed before for certain Ir(I) systems such as $\text{Ir}(\text{CO})_3\text{Cl}$,⁵⁶ $\text{Ir}(\text{CO})_2(\text{acac})$ (acac = acetylacetonato),⁵⁷ and $[\text{IrCl}(\text{PF}_3)_2]_2$.⁵⁸

The mixed carbonyl phosphine complex **3** is synthesized by either reacting **2** with PPh_3 or reacting **1** with CO in the presence of ca. 1 equiv of PPh_3 . Infrared and ^{31}P NMR spectroscopic data reveal the presence of both CO and PPh_3 coordinated to Ir(I). The room temperature ^1H NMR spectrum of a sample of **3** that is carefully prepared to have no excess PPh_3 displays two inequivalent methyl resonances and two inequivalent methylene resonances for the ethyl groups of the Et_2dtc ligand (see Table 4). With trace amounts of PPh_3 present, an ambient temperature ^1H NMR spectrum of **3** exhibits two broad resonances for the ethyl groups of the Et_2dtc ligand. Each of the broad signals decoalesces and sharpens at -50°C , appearing as two triplets and two quartets for the two inequivalent ethyl groups, while at 100°C the methyl signals appear as one triplet. The observed dynamic behavior is consistent with exchange via transient formation of $\text{Ir}(\text{PPh}_3)_2(\text{CO})(\text{Et}_2\text{dtc})$ and facile C-N bond rotation within that species.

A single crystal X-ray analysis of $\text{Ir}(\text{CO})(\text{PPh}_3)(\text{Et}_2\text{dtc})$ (**3**) confirms the coordination geometry of the complex assigned from the spectroscopic data, although it reveals considerable distortion from perfect planarity. A perspective drawing of complex **3** is shown in Figure 1, and important bond distances and angles are tabulated in Table 2. The Ir-S bond distances of 2.372(3) Å for S1 and 2.384(3) Å for S2 indicate a slight structural trans effect, while the similarity of S1-C1 and S2-C1 bond lengths indicate that the -1 charge of the dithiocarbamate is delocalized over both sulfur atoms. The Et_2dtc chelate

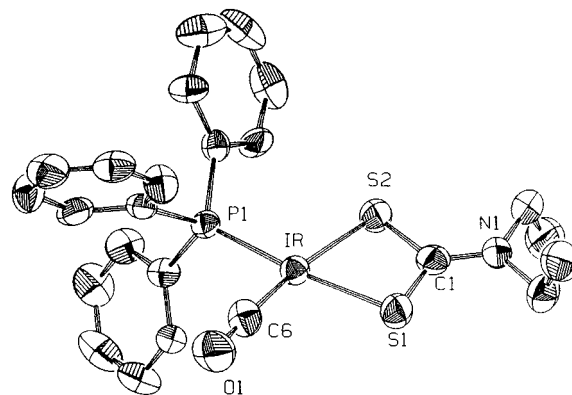


Figure 1. ORTEP drawing of $\text{Ir}(\text{CO})(\text{PPh}_3)(\text{Et}_2\text{dtc})$ (**3**). Thermal ellipsoids are shown at 50% probability.

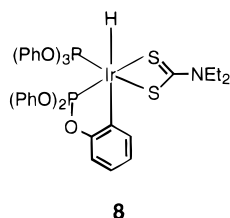
results in a S1-Ir-S2 bond angle of 74° , appreciably less than the idealized 90° value.

The syntheses of complexes **4-7** are relatively routine substitution reactions. All of the NMR data for these complexes are consistent with products having mirror symmetry in which any conformational effects are averaged out at room temperature. The chelating di(phosphines) dppe and dpfpe of **6** and **7** have multiplet resonances ca. 2 ppm indicating the equivalence of the four methylene protons in each complex. The ^{31}P NMR resonances of complexes **4-7** are all singlets. A benzene solution of the bis(triphenylphosphite) complex $\text{Ir}(\text{P}(\text{OPh})_3)_2(\text{Et}_2\text{dtc})$ (**5**) is not stable and yields the ortho-metalated species (**8**). The ^1H NMR spectrum of a benzene solution of **8** displays the hydride resonance at -16.02 ppm as a doublet of doublets ($^2J_{\text{H-P}} = 17.1, 24.9$ Hz) with coupling from two cis phosphorus nuclei. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows two doublets ($^2J_{\text{P-P}} = 21.8$ Hz) at 88.60 and 112.40 ppm consistent with cis phosphorus nuclei. Based on the NMR spectra, the stereochemistry of **8** can be assigned unambiguously as that shown below.

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Electronic Spectra of Complexes. Dilute solutions of Ir(I) Et₂dtc complexes are yellow in color, and their absorption spectra reveal maxima around 400 nm as given in Table 5. From the magnitude of the extinction coefficient, ϵ , the transition is charge transfer in character. A general trend emerges from Table 5 for the Ir(Et₂dtc)(diphosphine) complexes; the more electron withdrawing triphenylphosphite and dpfpe ligands result in absorbances that are higher energy than their triphenylphosphine and dppe counterparts. This simple correlation, however, cannot be extended to include those complexes containing CO and COD ligands.

Complexes **3**, **5**, and **6** exhibit luminescence in fluid solution at ambient temperature. Excitation of methylene chloride solutions of these complexes near 450 nm leads to broad and featureless emissions centered near 500 nm. Representative electronic and luminescence spectra are shown in Figure 2 for a dilute butyronitrile solution of Ir(CO)(PPh₃)(Et₂dtc). This represents the first example of luminescence from a four-coordinate Ir(I) complex in fluid solution. Like four-coordinate d⁸ dithiolate complexes of Ir(I) and Pt(II) that have been reported recently,^{13,14,19–28,31,34,59–61} all of the Et₂dtc complexes are photoluminescent in rigid media at 77 K. The spectra of the Ir(I) dithiocarbamate complexes, however, show a concentration dependence with low energy bands appearing with increasing concentration. The origin of absorption and emission from these complexes is currently under investigation and will be described in a future report.

Electrochemical Characterization of Complexes. The electrochemical properties of complexes **1–7** were investigated in the range of 1.5 to –1.2 V, and the results show irreversible oxidation waves in the cyclic voltammograms with peak potentials given in Table 5. The voltammograms for each compound were recorded using the same experimental parameters, and, therefore, some empirical conclusions may be drawn. The dicarbonyl complex Ir(CO)₂(Et₂dtc) has the highest peak oxidation potential of 1.111 V, reflecting the strong π -acid character of the carbonyl ligands. The oxidation is shifted to less positive potentials for Ir(CO)(PPh₃)(Et₂dtc) and Ir(PPh₃)₂(Et₂dtc) which display peak potentials of 0.966 and 0.490 V, respectively. The peak potential observed for Ir(dppe)(Et₂dtc) (0.544 V) is similar to that seen for Ir(PPh₃)₂(Et₂dtc) and is consistent with the P₂S₂ donor set for each. The complex Ir(P(OPh)₃)₂(Et₂dtc) has an oxidation peak potential of 0.857 V which is higher than that of the PPh₃ analog, as expected based on the electron donating ability of P(OPh)₃ vs PPh₃. A similar rationale can be used to account for the increase in peak potential from 0.544 to 0.932 V for Ir(dppe)(Et₂dtc) and Ir(dpfppe)(Et₂dtc), respectively. The results presented here show that as the ligand donor ability is changed systematically, the oxidation peak potential is altered in a consistent way. Specifically, the better the electron donation of ligand L + L', the more easily oxidized is the complex. This observation is

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Table 5. Room Temperature Electronic Spectral and Electrochemical Data for Ir(L)(L')(Et₂dtc) Complexes^a

complex	nm	$\times 10^3$ cm ⁻¹	ϵ_{\max} (M ⁻¹ cm ⁻¹)	E_p^{oxc} (V)
1 Ir(COD)(Et ₂ dtc)	406	24.6	1084	0.986
	446	22.4	1246	
	492	20.3	344	
2 Ir(CO) ₂ (Et ₂ dtc)	379	26.4	3100	1.111
	406	24.6	1950	
3 Ir(CO)(PPh ₃)(Et ₂ dtc)	400	25.0	3050	0.966
	445	22.5	1350	
4 Ir(PPh ₃) ₂ (Et ₂ dtc) ^b	365	27.4	6980	0.490
	451	22.2	3240	
5 Ir(P(OPh) ₃) ₂ (Et ₂ dtc) ^b	310	32.2	11050	0.857
	397	25.2	2630	
6 Ir(dppe)(Et ₂ dtc) ^c	345	29.0	6500	0.544
	431	23.2	2700	
7 Ir(dpfppe)(Et ₂ dtc) ^b	319	31.3	11080	0.932
	407	24.6	3540	

^a Electronic spectra recorded in chloroform unless otherwise noted.

^b Electronic spectrum recorded in methylene chloride. ^c Recorded in acetonitrile; values are vs NHE based on the Fc/Fc⁺ couple at 0.400 v as an internal standard.

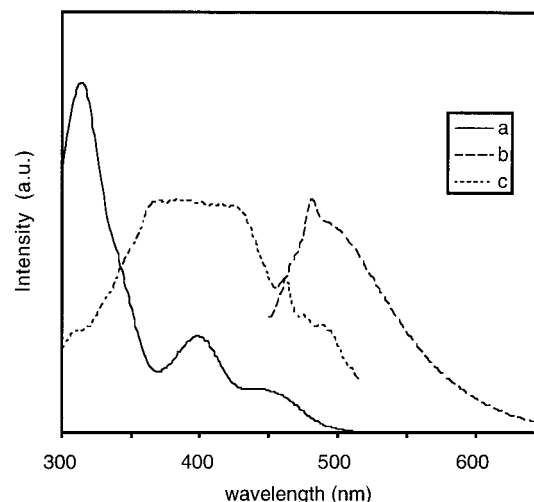


Figure 2. Ambient temperature absorption and luminescence spectra of a 8.2×10^{-5} M butyronitrile solution of Ir(CO)(PPh₃)(Et₂dtc) (**3**). a = absorption spectrum; c = excitation spectrum monitoring emission at 530 nm; b = emission spectrum with excitation at 425 nm.

consistent to a good extent with changes in the lowest energy absorbance of the different complexes (see Table 5). Similar behavior has been observed also for IrLL'(mnt)²⁻ complexes and indicates that the highest occupied orbital in these complexes has significant metal character which in turn is altered by the donicity of L + L'.⁶²

Reactions with Hydrogen. The oxidative addition of H₂ to three of the Ir(Et₂dtc) complexes has been investigated. When Ir(CO)(PPh₃)(Et₂dtc) (**3**) in C₆D₆ is placed under H₂ at 323 K, rapid reaction takes place leading to the formation of three dihydride complexes within 10 min, eq 2 and Figure 3a. From the coupling patterns of the hydride resonances, it is possible to assign the structure of each dihydride product unequivocally. Complex **9a** possesses hydride resonances at –6.11 and –15.70 ppm with similar ²J_{H–P} for each hydride corresponding to a fac arrangement of the phosphine and hydride ligands; only the structure shown as **9a** has this arrangement with inequivalence of the two hydrides. Complex **9b**, on the other hand, has one hydride trans to phosphorus leading to the observed splitting pattern with ²J_{H–P} of 166.5 Hz for the resonance at –7.74 ppm.

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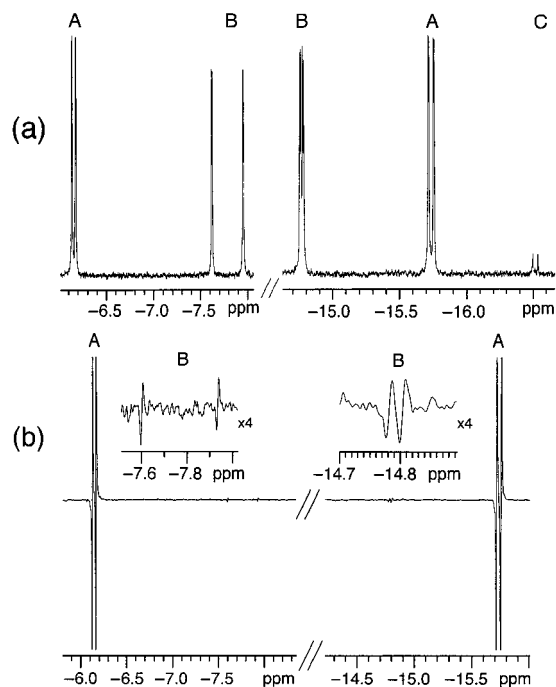
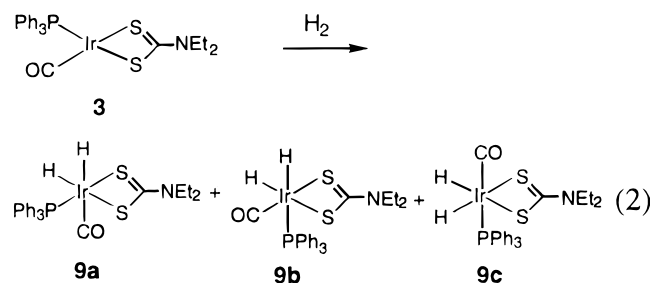


Figure 3. (a) Hydride region of the ^1H NMR spectrum for the addition of H_2 to $\text{Ir}(\text{CO})(\text{PPh}_3)(\text{Et}_2\text{dtc})$ (**3**). **A** = complex **9a**; **B** = complex **9b**; **C** = complex **9c**. (b) Hydride region of the ^1H NMR spectrum for the addition of para-enriched H_2 to $\text{Ir}(\text{CO})(\text{PPh}_3)(\text{Et}_2\text{dtc})$ (**3**). **A** = complex **9a**; **B** = complex **9b**. Kinetic selectivity shown is approximately 170:1 favoring **9a**.

The minor component of the product mixture, complex **9c**, has two equivalent hydrides and a fac arrangement for the phosphine and two hydrides; only the structure shown as **9c** is consistent with the observed resonances for that component. The ^{31}P NMR spectrum of the reaction solution supports the notion of only three isomeric dihydride products from the reaction.



In order to address the kinetic selectivity of H_2 oxidative addition to **3** in light of the known stereoselectivity of oxidative addition in the related $\text{IrX}(\text{CO})(\text{dppe})$ system,^{9,10} experiments involving parahydrogen induced polarization (PHIP) were conducted.^{63–71} In PHIP, oxidative addition reactions using

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hydrogen enriched in the para spin state lead to enhanced resonances of the product hydrides. For the reaction of **3** with $p\text{-H}_2$ at 298 K, a 40-fold enhancement of hydride resonances was seen mainly in complex **9a** with a kinetic selectivity for **9a** over **9b** of ca. 170:1 (Figure 3b). This kinetic selectivity corresponds to a $\Delta\Delta G^\ddagger$ for hydrogen oxidative addition of 3.3 kcal/mol. The addition of H_2 to form **9a** occurs over the S–Ir–CO axis of **3** with the CO and S donors moving to positions cis to each other and trans to the hydride ligands. The observed kinetic selectivity to form **9a** is larger than that observed for H_2 addition over the P–Ir–CO axis of $\text{Ir}(\text{CO})\text{X}(\text{dppe})$ (X = Cl, Br, and I).^{9,10}

The basis of the stereoselectivity in H_2 oxidative addition has been much discussed.^{3–8,72,73} As with the kinetic isomer of H_2 addition to $\text{Ir}(\text{CO})\text{X}(\text{dppe})$, isomer **9a** corresponds to addition with H_2 over the axis of the starting square planar complex that contains the CO ligand.^{9,10} As the addition proceeds, the entering H_2 molecule, the CO moiety, and the ligand initially trans to it move into positions corresponding to the equatorial sites of a trigonal bipyramid intermediate. The CO ligand in this site can through backbonding reduce the repulsive interaction between the filled Ir d_{z^2} orbital and the filled σ^b function of the H_2 molecule. This repulsive interaction has been cited as the major contributor to the activation barrier for H_2 oxidative addition to d^8 complexes.⁷ Based on the results for H_2 addition to **3** and the previous report of H_2 addition to $\text{Ir}(\text{CO})\text{X}(\text{dppe})$, it seems evident that the carbonyl ligand properly located in the reaction intermediate reduces the activation barrier effectively, leading to the observed stereoselectivity of oxidative addition.

Transfer of parahydrogen induced polarization to ^{31}P was also achieved using the INEPT+ pulse sequence, as has been described previously,⁶⁸ leading to enhancement of the ^{31}P resonance for **9a**. While isomer **9c** is not expected to exhibit polarization because PHIP requires inequivalence of the added hydrogens, it is also not anticipated to be a primary kinetic product from a cis concerted addition owing to constraints of the Et_2dtc chelate ring. In such an H_2 oxidative addition reaction, the two ligands trans to the hydrides in the product (and cis to each other) originate in the reactant as mutually trans, but because of Et_2dtc chelation, this is not possible in **9c**. The kinetic selectivity of the reaction was confirmed when the reaction was carried out at 298 K rather than at 323 K; only complex **9a** was observed to form in the first 10 min. After 20 h at 298 K, however, a product distribution similar to that of Figure 3a was found.

In light of recent studies that have used HMQC methods in conjunction with parahydrogen induced polarization to see heteronuclear resonances rapidly and efficiently,^{64,74,75} we have carried out HMQC experiments to observe the ^{31}P signals of **9a** and **9b**. The HMQC approach is superior to the INEPT+ polarization transfer experiment reported by us previously since it detects ^{31}P indirectly through the ^1H resonances, thereby making optimal use of parahydrogen enhancements. As expected, the HMQC spectrum displays four cross peaks correlating the phosphorus signals of **9a** and **9b** at 15.6 and 4.6 ppm with their respective hydride resonances, as shown in Figure 4a.

(71) Eiseenschmid, T. C.; McDonald, J.; Eisenberg, R. *J. Am. Chem. Soc.* **1989**, *111*, 7267–7269.

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(75) Duckett, S. B.; Mawby, R. J.; Partridge, M. P. *J. Chem. Soc., Chem. Commun.* **1996**, 383–384.

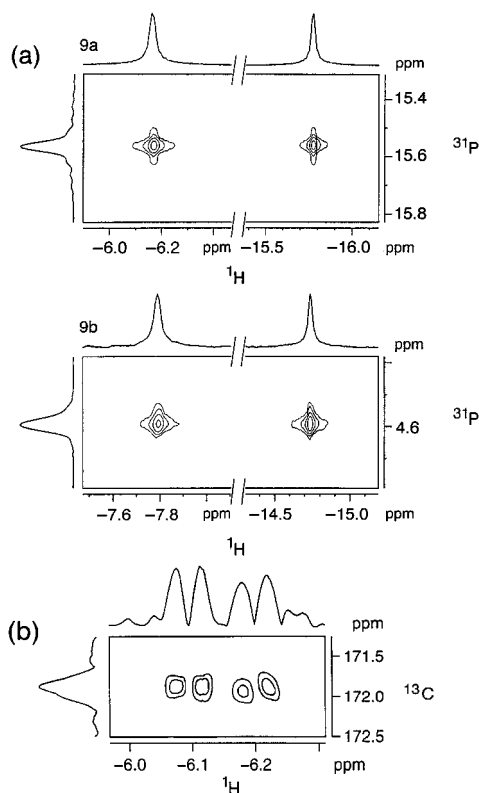


Figure 4. (a) The HMQC spectrum correlating the ^{31}P signals of **9a** and **9b** at 15.6 and 4.6 ppm with their respective hydride resonances. (b) The ^1H - ^{13}C gradient assisted correlation spectrum of **9a** in *neat* C_6H_6 displaying carbonyl (^{13}C) and hydride (^1H) regions.

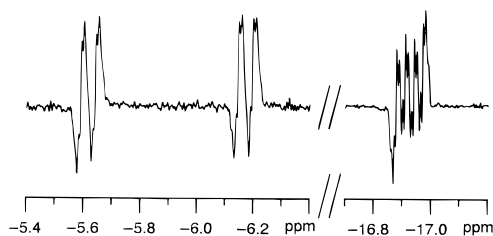


Figure 5. Hydride region of the ^1H NMR spectrum for the addition of para-enriched H_2 to $\text{Ir}(\text{dppe})(\text{Et}_2\text{dtc})$ (**7**). Signal centered at -5.92 ppm originates from hydride trans to phosphorus.

The HMQC experiment was also used in conjunction with a z-field gradients to observe the natural abundance ^{13}C resonance of the carbonyl ligand in a submilligram sample of **9a** in *neat* C_6H_6 . Figure 4b shows the ^1H - ^{13}C gradients-assisted correlation spectrum. The cross peak connecting the hydride, (^1H) -6.1 ppm, and carbonyl carbon, (^{13}C) 172 ppm, is observed clearly in under 2 min. The advantages of using z-field gradients are that it reduces the phase cycling requirements of the NMR experiment, enabling two scans per increment to be used and importantly in this case, it acts as a spectroscopic filter to remove signals not involved in the ^1H - ^{13}C - ^1H coherence pathway. The latter establishes that p- H_2 effects can be used to monitor reactions in protio solvents.

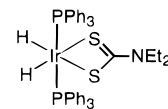
Dipolar relaxation and the NOESY experiment can also be used in conjunction with parahydrogen polarization to obtain information about ligand exchange processes.⁷⁶ A series of NOESY spectra collected on toluene- d_8 solutions of **3** and p- H_2 with varying amounts of PPh_3 , mixing times of 500 or 300 ms and total acquisition times of 20 min yielded cross peaks resulting from magnetization transfer from p- H_2 enhanced

Table 6. Relative Cross Peak Intensities for the Interconversion of the Hydrides of $\text{IrH}_2(\text{CO})(\text{PPh}_3)(\text{Et}_2\text{dtc})$, **9b**, as a Percent of the Diagonal Peak Intensity

$[\text{PPh}_3]$	% intensity	k_{obs} (s^{-1})
0	39	0.55
3	36	0.52
45	23	0.37
75	20	0.33

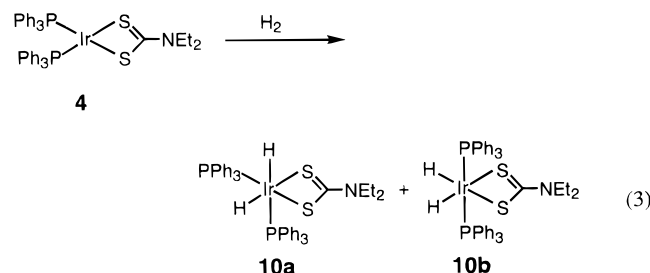
resonances. In this experiment, positive cross peaks reveal chemical exchange between sites, while negative cross peaks arise through NOE and connect nuclei that are close in space. A toluene- d_8 solution of complex **9a**, with no added PPh_3 at 353 K, displays NOE cross peaks between the two hydride ligands and between the hydride ligands and the ortho phenyl protons of bound PPh_3 , while exchange cross peaks are observed correlating the hydride ligands to free H_2 . Only on warming to 358 K does the corresponding NOESY spectrum with short mixing times reveal exchange cross peaks between each hydride ligand of **9a** and each hydride ligand of **9b**, indicative of a nonstereospecific exchange process.

At 353 K, the hydride ligands of **9b** show no correlation with the corresponding ortho phenyl protons of coordinated PPh_3 or to free H_2 , although the two hydride ligands are observed to undergo exchange with each other. Furthermore, for a given mixing time, an increase in the concentration of free PPh_3 from zero to a 75-fold excess results in a progressive decrease in the intensity of the intramolecular exchange peaks between the hydride ligands of **9b**. Standard methods were used to obtain values of k_{obs} (s^{-1}) for this exchange process and are shown for a variety of PPh_3 concentrations in Table 6.⁷⁷ The concentration dependence of PPh_3 vs cross peak intensity suggests that the process interconverting the hydride ligands in **9b** proceeds initially with phosphine dissociation. Additionally, the observation of a hydride-hydride cross peak indicates that the hydride ligands retain distinct magnetic identities in the resultant $16 e^-$ intermediate. In these experiments, the time for which p- H_2 enhancements are observable decreases as the concentration of PPh_3 is increased. At the same time, a new dihydride species, $\text{IrH}_2(\text{PPh}_3)_2(\text{Et}_2\text{dtc})$ (**10b**), is observed to form from **9**, presumably via CO dissociation from **9** and PPh_3 coordination to the unsaturated Ir(III) intermediate.



10b

The addition of H_2 to a toluene- d_8 solution of **4** results in the formation of two dihydride containing complexes according to eq 3. The complexes, $\text{IrH}_2(\text{PPh}_3)_2(\text{Et}_2\text{dtc})$ (**10a** and **10b**) exist



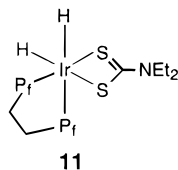
in two forms: one with inequivalent hydrides (**10a**) and a second with equivalent hydrides and trans phosphines (**10b**). The

(76) Sleight, C. J.; Duckett, S. B.; Messerle, B. A. *Chem. Commun.* **1996**, 2395–2396.

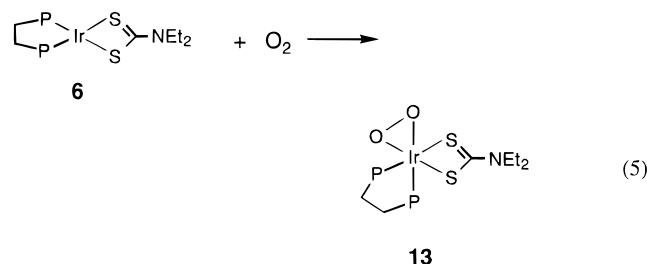
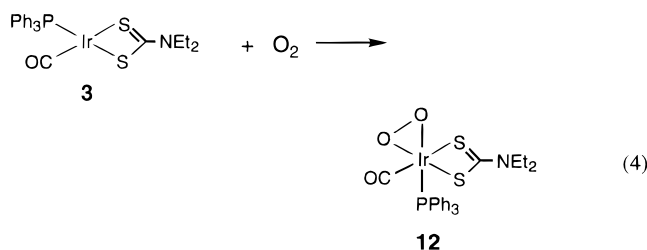
(77) Bodenhausen, G.; Ernst, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 1304.

hydride trans to phosphorus of **10a** is centered at -9.21 ppm and possesses a large trans phosphorus coupling constant ($^2J_{\text{H-P}}$ of 156.6 Hz) and a smaller cis phosphorus coupling constant ($^2J_{\text{H-P}}$ of 22.6 Hz), while the hydride trans to sulfur appears as a doublet of doublet of doublets at -17.35 ppm displaying two cis phosphorus coupling constants and a small hydride coupling constant ($^2J_{\text{P-H}} = 14.0$, $^2J_{\text{P-H}} = 18.0$, $^2J_{\text{H-H}} = 3.7$ Hz). The two equivalent hydrides of **10b** appear at -18.44 ppm as a triplet with a small $^2J_{\text{H-P}}$ of 16.8 Hz consistent with a cis hydride-phosphorus disposition. When $\text{Ir}(\text{PPh}_3)_2(\text{Et}_2\text{dtc})$, **4**, reacts with $p\text{-H}_2$ at 300 K, enhanced resonances are seen for **10a**, but the size of the parahydrogen enhancement drops to zero as **10b** is formed. Complex **10b** is not observed to lose H_2 upon heating to temperatures as high as 358 K.

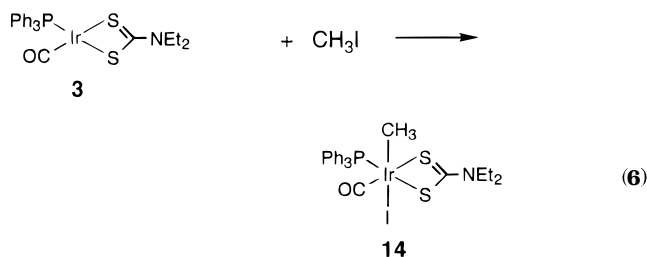
Polarization is also seen in the ^1H NMR resulting from oxidative addition of para-enriched H_2 to $\text{Ir}(\text{dpfpe})(\text{Et}_2\text{dtc})$ as shown in Figure 5. The hydride trans to phosphorus is centered at -5.92 ppm with a large $^2J_{\text{H-P}}$ of 219 Hz, while the hydride trans to sulfur is shifted significantly to higher field appearing as a multiplet at -16.88 ppm. The complicated splitting patterns for both hydride ligands are interpreted as involving coupling to the adjacent hydride, two phosphorus nuclei and fluorines in the dpfpe ligand (see Table 4).



Reactions with Oxygen. Both $\text{Ir}(\text{CO})(\text{PPh}_3)(\text{Et}_2\text{dtc})$ and $\text{Ir}(\text{dppe})(\text{Et}_2\text{dtc})$ are found to react rapidly in solution with molecular oxygen as shown in eqs 4 and 5, respectively. The yellow color of the solution fades as the reaction proceeds, indicating that oxidation to an Ir(III) species has occurred. The resonances of the dithiocarbamate ligand observed in ^1H NMR spectra of the O_2 adducts differ considerably from those of the respective starting compounds. For $\text{Ir}(\text{O}_2)(\text{CO})(\text{PPh}_3)(\text{Et}_2\text{dtc})$ (**12**), the dithiocarbamate methyl groups appear as two inequivalent triplets while the methylene protons exhibit three distinct multiplets in a ratio of 1:1:2 corresponding to four inequivalent methylene protons (two signals have overlapping chemical shifts). Given that solutions of **12** display distinct methyl and methylene resonances we conclude that rotation around the C–N bond in the Et_2dtc ligand is slow on the NMR time scale. The structure of **12** has not been unambiguously assigned with the point of uncertainty being the relative disposition of the CO and PPh_3 ligands but is displayed in eq 4 based on $^31\text{P}\{^1\text{H}\}$ NMR spectral comparison to that found for **9a** and **9b**. The $^31\text{P}\{^1\text{H}\}$ spectrum of $\text{Ir}(\text{O}_2)(\text{dppe})(\text{Et}_2\text{dtc})$ (**13**) contains two signals with unresolved cis phosphorus coupling. The oxygen is bound most likely sideways to the Ir center in both complexes in analogy with Vaska-type examples.^{78,79} Further characterization of the O_2 adducts comes from infrared spectroscopy which shows bands at 843 and 818 cm^{-1} for $\text{Ir}(\text{O}_2)(\text{CO})(\text{PPh}_3)(\text{Et}_2\text{dtc})$ and $\text{Ir}(\text{O}_2)(\text{dppe})(\text{Et}_2\text{dtc})$, respectively, consistent with $\eta^2\text{-O}_2$. The O_2 adducts are stable under vacuum. However, both compounds lose O_2 upon UV photolysis in solution. Some starting material is formed, although there appears to be considerable decomposition, the products of which have yet to be identified.

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Reaction with Methyl Iodide. The addition of methyl iodide to an acetone solution of $\text{Ir}(\text{CO})(\text{PPh}_3)(\text{Et}_2\text{dtc})$ (**3**) yields $\text{Ir}(\text{CH}_3)(\text{CO})(\text{I})(\text{PPh}_3)(\text{Et}_2\text{dtc})$ (**14**) in 88% yield. The infrared spectrum displays ν_{CO} at 2025 cm^{-1} consistent with the presence of a terminal carbonyl ligand coordinated to Ir(III), while the ^1H NMR spectrum shows the methyl ligand as a doublet with a small $^3J_{\text{H-P}}$ of 4.1 Hz consistent with *cis*-methyl- and triphenylphosphine ligands. Although the stereochemistry of **14** has not been unambiguously assigned, strong precedence exists for trans oxidative addition of methyl iodide to other four-coordinate complexes of Ir(I).⁸⁰ Therefore, we assign the stereochemistry of **14** to that shown in eq 6 with methyl and iodide ligands having trans dispositions.



Conclusions

The preparation of and characterization of neutral Ir(I) *N,N'*-diethyldithiocarbamate complexes have been reported. The complexes are easily prepared via substitution reactions from $\text{Ir}(\text{COD})(\text{Et}_2\text{dtc})$ and form stable four-coordinate species as determined spectroscopically and from a single crystal X-ray diffraction study of $\text{Ir}(\text{CO})(\text{PPh}_3)(\text{Et}_2\text{dtc})$. Remarkably, $\text{Ir}(\text{CO})(\text{PPh}_3)(\text{Et}_2\text{dtc})$, $\text{Ir}(\text{dppe})(\text{Et}_2\text{dtc})$, and $\text{Ir}(\text{P}(\text{OPh})_3)_2(\text{Et}_2\text{dtc})$ are luminescent in fluid solution, and all complexes are emissive in low temperature glasses. Their luminescence behavior is similar to that observed for Pt(II) dithiolate complexes although the nature of the excited state is not clear at this time.

The complex $\text{Ir}(\text{CO})(\text{PPh}_3)(\text{Et}_2\text{dtc})$ (**3**) exhibits great similarity to Vaska's complex, $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$, in terms of its reaction chemistry. Complex **3** oxidatively adds H_2 and MeI and readily forms an adduct with O_2 in solution and in the solid state. Because of the *cis* nature of H_2 oxidative addition and the presence of the dithiocarbamate chelate, there are more stereochemical consequences to the dihydride products $\text{IrH}_2(\text{CO})(\text{PPh}_3)(\text{Et}_2\text{dtc})$ (**9**) than for the corresponding addition product to $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$. It is found that H_2 addition to $\text{Ir}(\text{CO})(\text{PPh}_3)(\text{Et}_2\text{dtc})$ occurs stereoselectively, as determined by

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exposure to para-enriched hydrogen, and displays a kinetic preference for H₂ addition over the S–Ir–CO axis. HMQC experiments in conjunction with parahydrogen induced polarization reveal both ³¹P and natural abundance ¹³CO ligation in very short acquisition times with submilligram samples. A NOESY experiment reveals intermolecular phosphine exchange concomitant with hydride equilibration for one of the systems, **9b**. The O₂ adducts Ir(O₂)(CO)(PPh₃)(Et₂dtc) and Ir(O₂)(dppe)(Et₂dtc) form readily in fluid solution and the solid state. However, they do not lose O₂ thermally and must be photolyzed to liberate oxygen.

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Supporting Information Available: Tables of data collection and refinement parameters, thermal parameters, atomic positional parameters, and complete bond distances and angles for non-hydrogen atoms for **3** (8 pages). See any current masthead page for ordering and Internet access instructions.

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