Studies of the Synthesis and Thermochemistry of Coordinatively Unsaturated Chelate Complexes (η^5-C_5Me_5)IrL_2 (L_2 = $TsNCH_2CH_2NTs$, $TsNCH_2CO_2$, CO_2CO_2)

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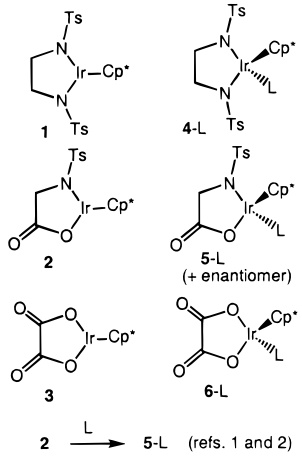
A comparative synthetic, structural, and thermochemical study on a series of chelate complexes containing the fragment (η^5-C_5Me_5)Ir [(η^5-C_5Me_5)Ir($TsNCH_2CH_2NTs$) (**1**), (η^5-C_5Me_5)Ir($TsNCH_2CO_2$) (**2**), (η^5-C_5Me_5)Ir(CO_2-CO_2) (**3**)] was performed to clarify the roles of carboxylato and sulfonamido ligands. Whereas **1** and **2** are monomeric in solution and in the solid state, **3** appears to exist as an oligomer or polymer, $(\mathbf{3})_n$, which can be broken up by addition of a ligand L such as a phosphine, CO, or 2-methoxypyridine to form (η^5-C_5Me_5)Ir(L)(CO_2-CO_2) (**6**). The synthesis of $(\mathbf{3})_n$ from [(η^5-C_5Me_5)IrCl(μ-Cl)]$_2$ required the use of silver oxalate in CH_3CN, but if other solvents were used, the bridging oxalato complex (η^5-C_5Me_5)IrCl(μ-η^2-η^2-C_2O_4)ClIr(η^5-C_5Me_5) (**7**) was obtained and identified by X-ray diffraction. Enthalpies for reaction of THF-soluble monomers **1** and **2** with PMe_3 were determined to be −28.7(0.5) and −28.5(0.4) kcal mol^{-1}, respectively. The oligomerization behavior of **3** may be a result of reduced σ- or π-donation of carboxylato ligands compared to *N*-tosylamido ligands, because the values for ν_{CO} in oxalato and bissulfonamido complexes **6**−CO and (η^5-C_5Me_5)Ir(CO)($TsNCH_2CH_2$-NTs) (**4**−CO) were 2064 and 2042 cm^{-1}, respectively.

Introduction

Here we report a comparative synthetic, structural, and thermochemical study on a series of chelate complexes containing the metal fragment (η^5-C_5Me_5)Ir^{III} (**1**, **2**, and **3**). In 1994, Grotjahn et al. reported a series of amino acid complexes featuring Cp*Ir bound to an *N*-acyl or *N*-tosyl amino acid ligand, deprotonated at N and carboxylate O.[1] These complexes, represented by *N*-tosylamidoglycine derivative **2**, were noteworthy for their high stability, coordinative unsaturation, and rapid, stereoselective ligand additions when chiral amino acids were involved.[1−3] Spectroscopic and X-ray crystallographic evidence pointed to significant π-donation from the acylated or tosylated nitrogen in **2**, which was reduced upon addition of a ligand L and formation of **5** (Scheme 1).[1,2] Even though some π-donation from the carboxylato oxygen was assumed, no direct evidence of this was available. Because sulfonamido ligands are increasingly important in organometallic chemistry,[4] it seemed important to clarify structure and bonding in complexes of type **2**. Although π-donation from N or O ligands is now a well-established phenomenon,[5] the synthesis and study of the title series of electronically and coordinatively unsaturated (η^5-C_5Me_5)Ir complexes (**1**−**3**) were expected to provide new insights into the bonding in **2**. Specifically, by comparing compounds with η^2-(*N*,*N*)-bis(sulfonamido), η^2-(*N*,*O*)-sulfonamidocarboxylato, and η^2-(*O*,*O*)-oxalato ligands (structures **1**, **2**, and **3**, respectively), we expected to determine the relative π-donating characteristics of the sulfonamido and carboxylato ligands. As described below, complete comparison of **3** with **1** and **2** was precluded by the unusual oligomerization and solubility behavior of **3**. However, all three compounds gave

Scheme 1



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corresponding CO adducts (**4**−CO, **5**−CO, and **6**−CO), whose IR spectroscopic data showed that π-donation of carboxylato ligands is less than that of *N*-tosylamido ligands.

Experimental Section

General Procedures. Unless otherwise specified, NMR spectra were recorded at 200, 300, 400, or 500 MHz with Varian spectrometers at room temperature. ^{1}H and ^{13}C NMR chemical shifts are reported in parts per million downfield from tetramethylsilane and referenced to residual solvent resonances (^{1}H NMR, 7.27 for C*H*Cl$_3$ in CDCl$_3$; ^{13}C NMR, 77.00 for *C*DCl$_3$), where ^{1}H NMR signals are given followed by multiplicity, coupling constants *J* in hertz, and integration in parentheses. For complex coupling patterns, the first coupling constant listed corresponds to the first splitting listed; e.g., for (dt, $J = 3.2$, 7.9, 1 H) the doublet exhibits the 3.2 Hz coupling constant. ^{31}P{^{1}H} NMR chemical shifts were referenced to external 85% H_3PO_4(aq).

IR spectra were obtained on either a Perkin-Elmer series 1600 or a Mattson Instruments model 2020 Galaxy series FT-IR spectrophotometer. Elemental analyses were performed at NuMega Resonance Labs (San Diego), Atlantic Microlab, Inc. (Georgia), or the Department of Chemistry, Arizona State University.

^{1}H and ^{13}C{^{1}H} NMR and IR data (ν_{CO}) for the chelated complexes are listed in Table 1.

Synthesis of 1. A 50 mL Schlenk flask was charged with a stirbar, TsNHCH$_2$CH$_2$NHTs[6] (53.9 mg, 0.146 mmol), [(η^5-C$_5$Me$_5$)IrCl(μ-Cl)]$_2$[7] (58.0 mg, 0.0728 mmol), and K_2CO_3 (40.5 mg, 0.293 mmol), and the flask was evacuated and filled with nitrogen. THF (10 mL) was then added via syringe under N_2. The resulting orange-yellow mixture was allowed to stir for 36 h at room temperature, after which time the color had changed to dark red. The solvent was removed on a high vacuum line to afford a red residue along with some pale green crystalline solid. A portion of CH_2Cl_2 (about 5 mL) was used to dissolve the residue, and the resulting solution was washed with an equal amount of H_2O and then concentrated on a high-vacuum line. The residue was purified by recrystallization from CH_2Cl_2−Et_2O, followed by refrigeration at −15 °C to give the title complex as dark red needles (99.0 mg, 98%): IR (KBr) 2918, 2859, 1599, 1495, 1447 cm^{-1}. Anal. Calcd for $C_{26}H_{33}IrN_2O_4S_2$ (693.92): C, 45.00; H, 4.80; N, 4.04. Found: C, 44.84; H, 4.76; N, 4.01.

Addition of PMe$_3$ to 1 To Give 4−PMe$_3$. In a glovebox, a flame-dried J. Young NMR tube was charged with **1** (12.6 mg, 0.0182 mmol) and CDCl$_3$ (0.7 mL) to make a dark red solution. To this solution was added PMe$_3$ (in excess), and a yellow solution resulted immediately. The reaction mixture was then subjected to chromatography with a Chromatotron (SiO_2, EtOAc−hexanes, 1:1) to give the title complex (13.4 mg, 96%) as a yellow solid: ^{31}P{^{1}H} NMR (202.3 MHz, CDCl$_3$) δ 26.01; IR (KBr) 2917, 1269, 1136 cm^{-1}. Anal. Calcd for $C_{29}H_{42}IrN_2O_4PS_2$ (769.99): C, 45.24; H, 5.50; N, 3.64. Found: C, 44.09; H, 5.42; N, 3.9.

Synthesis of 7 [(η^5-C$_5$Me$_5$)IrCl(μ-η^2-η^2-C$_2$O$_4$)ClIr(η^5-C$_5$Me$_5$)]. In the glovebox, a 50 mL Schlenk flask was charged with a stirbar, [(η^5-C$_5$Me$_5$)IrCl(μ-Cl)]$_2$ (115.0 mg, 0.144 mmol), and $Ag_2C_2O_4$ (46.6 mg, 0.153 mmol, 1.07 equiv), and THF (20 mL) was added. The mixture was stirred for 4 d, after which time it was noted that the mixture had lightened somewhat from orange to yellow, but that most of the yellow color was in the solid phase. Therefore, CH_3CN (20 mL) was added, and the mixture was stirred for an additional 13 h, after which more but not all color was in the solution. The mixture was filtered in air through a pad of Celite in a fritted funnel, and the filter cake was washed with warm CH_3CN, followed by CH_2Cl_2 in several portions. Combined filtrates were concentrated by rotary evaporation, and the yellow solid residue (135 mg) was recrystallized from CH_2Cl_2−THF, allowing the solvent to slowly evaporate through a syringe needle in a septum. Pale orange crystals of **7** (102.0 mg, 87%) were isolated. Suitable single crystals for X-ray diffraction were obtained by recrystallization from CH_2Cl_2−THF: mp 298 °C dec; (when sample heated starting at 286 °C); IR (KBr) 1620 cm^{-1} (vs); ^{1}H NMR (CDCl$_3$) δ 1.62 (s). Anal. Calcd for $C_{22}H_{30}Cl_2Ir_2O_4$ (813.86): C, 32.46; H, 3.72. Found: C, 32.43; H, 3.67.

Synthesis of (3)$_n$. To a stirred suspension of [(η^5-C$_5$Me$_5$)IrCl(μ-Cl)]$_2$ (257.7 mg, 0.323 mmol) in CH_3CN (3 mL) in the glovebox was added $Ag_2C_2O_4$ (229.6 mg, 0.756 mmol, 1.17 equiv). The mixture was stirred for 39 h before it was diluted with an equal volume of CH_2Cl_2 and filtered through Celite, and the filter cake was rinsed with CH_2Cl_2 in portions. Combined filtrates were concentrated by rotary evaporation. To the yellow syrupy residue was added CH_2Cl_2, and the resulting mixture was concentrated. To the residue were added CH_2Cl_2 and THF, and some of the solvent was allowed to evaporate slowly. The supernatant was pipetted away, and the remaining yellow solid was stored over P_4O_{10} under vacuum, leaving 232.0 mg (78%): IR (KBr) 1699, 1675, 1633, 1595 cm^{-1} (all vs). Anal. Calcd for $C_{12}H_{15}IrO_4 \cdot 0.5CH_2Cl_2$ (415.49 + 42.47): C, 32.79; H, 3.52. Found: C, 32.88; H, 3.47.

Addition of PMe$_3$ to (3)$_n$ To Give 6−PMe$_3$. To a suspension of (**3**)$_n \cdot 0.5CH_2Cl_2$ (16.7 mg, 0.0349 mmol) in CDCl$_3$ (ca. 1 mL) in a J. Young NMR tube was added PMe$_3$ (4.5 μL). Not all cloudiness disappeared on addition of the phosphine, so an additional 1.0 μL was added (total 5.5 μL, 0.053 mmol). After acquisition of NMR spectra the contents of the tube were filtered through a cotton plug in a pipet, the cotton rinsed with CH_2Cl_2, and the filtrate concentrated to leave a yellow solid (12.9 mg, 0.0262 mmol, 75%). Anal. Calcd for $C_{15}H_{24}IrO_4P$ (491.55): C, 36.65; H, 4.92. Found: C, 36.53; H, 4.90.

Addition of PEt$_3$ to (3)$_n$ To Give 6−PEt$_3$. In a manner similar to that used to make **6**−PMe$_3$, a suspension of (**3**)$_n \cdot 0.5CH_2Cl_2$ (14.8 mg, 0.0323 mmol) in CDCl$_3$ (ca. 1 mL) in an NMR tube was treated with PEt$_3$ (4.0 mg, 0.034 mmol). Not all cloudiness disappeared on addition of the phosphine, so an additional 1.0 μL was added (total ca. 0.04 mmol). The presence of the product was shown by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopies. Filtration and recrystallization from CDCl$_3$−CH_2Cl_2−hexane provided yellow crystals of **6**−PEt$_3$ (16.5 mg, 96%): mp 248 °C dec (apparatus preheated to 240 °C); ^{31}P{^{1}H} NMR (CDCl$_3$, 80.95 MHz) δ 7.46. Anal. Calcd for $C_{18}H_{30}IrO_4P$ (533.63): C, 40.52; H, 5.67. Found: C, 40.46; H, 5.64.

Addition of PPh$_3$ to (3)$_n$ To Give 6−PPh$_3$. In a manner similar to that used to make **6**−PMe$_3$, a suspension of (**3**)$_n \cdot 0.5CH_2Cl_2$ (14.8 mg, 0.0323 mmol) in CDCl$_3$ (ca. 1 mL) in an NMR tube was treated with PPh$_3$ (9.0 mg, 0.034 mmol). The presence of the product was shown by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopies. Filtration and recrystallization from CDCl$_3$−CH_2Cl_2−hexane provided yellow crystals of **6**−PPh$_3$ (21.3 mg, 97%): mp 253 °C dec (apparatus preheated to 236 °C). Anal. Calcd for $C_{30}H_{30}IrO_4P$ (677.76): C, 53.16; H, 4.46. Found: C, 52.79; H, 4.29.

Addition of 2-Methoxypyridine to (3)$_n$ To Give 6−NC$_5$H$_4$OMe. In a way manner to that used to make **6**−PMe$_3$, a suspension of (**3**)$_n \cdot 0.5CH_2Cl_2$ (46.6 mg, 0.112 mmol) in CH_2Cl_2 (ca. 1 mL) in a vial was treated with 2-methoxypyridine (22.4 mg, 0.205 mmol). Within 2 min a slightly cloudy yellow solution formed. The mixture was filtered through a bit of Celite on a glass wool plug in a pipet, and the Celite was rinsed with additional CH_2Cl_2. The filtrates were concentrated by rotary evaporation and the yellow residue stored under oil pump vacuum, leaving yellow solid **6**−NC$_5$H$_4$OMe (51.8 mg, 88%). Anal. Calcd for $C_{18}H_{22}IrNO_5$ (524.60): C, 41.21; H, 4.23; N, 2.67. Found: C, 40.75; H, 3.96; N, 2.61.

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Table 1. ^{1}H and ^{13}C{^{1}H} NMR and IR Data for Chelate Complexes[a]

	^{1}H			^{13}C{^{1}H}				
complex	$C_5(CH_3)_5$	chelate	L	$C_5(CH_3)_5$	$C_5(CH_3)_5$	chelate	L	IR (KBr, cm^{-1}) ν_{CO}
1	1.78 (s, 15 H)	2.39 (s, 6 H, Ar−C*H*$_3$) 2.76 (s, 4 H, C*H*$_2$C*H*$_2$) 7.20 (d, *J* = 8.0, 4 H) 7.63 (d, *J* = 8.0, 4 H)		89.63	10.34	21.37 (Ar−*C*H$_3$) 53.95 (*C*H$_2$*C*H$_2$) 127.15, 129.46 (H−*C*$_{Ar}$) 139.65, 142.08 (*C*$_{Ar}$)		
2[b]	1.81 (s, 15 H)	2.40 (s, 3 H, Ar−C*H*$_3$) 3.35 (s, 2 H, NC*H*$_2$CO) 7.26 (d, *J* = 8, 2 H) 7.64 (d, *J* = 8, 2 H)		87.7	9.9	21.2 (Ar−*C*H$_3$) 52.9 (N*C*H$_2$CO$_2$) 127.4, 129.7 (H−*C*$_{Ar}$) 136.3, 143.2 (*C*$_{Ar}$) 186.0 (*C*═O)		1684
(**3**)$_n$	1.66 (s, 15 H)			ND[c]	ND[c]	ND[c]		1595, 1633, 1675, 1699
4−PMe$_3$	1.78 (d, *J* = 2.0, 15 H)	2.27 (m, 2 H) 2.36 (s, 6 H) 2.72 (m, 2 H) 7.17 (d, *J* = 8.1, 4 H) 7.66 (d, *J* = 8.1, 4 H)	1.85 (d, *J* = 9.8, 9 H)	ND	ND	ND	ND	
4−CO	1.99 (s, 15 H)	2.32−2.38 (m, 2 H) 2.39 (s, 6 H) 2.58−2.66 (m, 2 H) 7.18 (d, *J* = 8, 2 H) 7.62 (d, *J* = 8, 2 H)		101.64	9.48	21.39 (Ar−*C*H$_3$) 54.84 (*C*H$_2$*C*H$_2$) 127.72, 129.16 (H−*C*$_{Ar}$) 137.28, 141.62 (*C*$_{Ar}$)	167.96 (*C*O)	2042[d]
5−PMe$_3$[b]	1.72 (d, *J* = 2.1, 15 H)	2.36 (s, 3 H) 3.70 (d, *J* = 16.5, 1 H) 3.95 (d, *J* = 16.5, 1 H) 7.20 (d, *J* ≈ 8, 2 H) 7.62 (d, *J* ≈ 8, 2 H)	1.59 (d, *J* = 11.0, 9 H)	91.3 (d, *J* = 2.3)	9.3	21.1 (Ar−*C*H$_3$) 52.9 (N*C*H$_2$CO$_2$) 127.0, 129.2 (H−*C*$_{Ar}$) 139.7, 141.4 (*C*$_{Ar}$) 185.1 (*C*O$_2$)	13.8 (d, *J* = 37.8, P*C*H$_3$)	1650 (OC═O)
5−CO[b]	1.94 (s, 15 H)	2.40 (s, 3 H) 3.54 (d, *J* = 16.6, 1 H) 3.79 (d, *J* = 16.6, 1 H) 7.25 (d, *J* = 8.2, 2 H) 7.68 (d, *J* = 8.2, 2 H)		100.9	9.0	21.2 (Ar−*C*H$_3$) 53.9 (N*C*H$_2$CO$_2$) 128.1, 129.7 (H−*C*$_{Ar}$) 135.9, 142.7 (*C*$_{Ar}$) 185.0 (*C*O$_2$)	169.2 (*C*O)	1671 (OC═O) 2033 (CO) 1651[d,e] (OC═O) 2049[d,e] (CO)
6−PMe$_3$	1.64 (d, *J* = 1.5, 15 H)		1.44 (d, *J* = 11.2)	90.10	8.95	165.63 (*C*O$_2$*C*O$_2$)	12.47 (d, *J* = 35.2, P*C*H$_3$)	1677, 1698
6−PEt$_3$	1.64 (d, *J* = 1.7, 15 H)		1.75 (quintet, *J* = 7.7, 6 H) 1.04 (dt, *J* = 16, 7.6, 9 H)	90.08 (d, *J* = 3.0)	8.77	165.76 (*C*O$_2$*C*O$_2$)	12.85 (d, *J* = 32.8, P*C*H$_2$) 6.34 (d, *J* = 3.1, PCH$_2$*C*H$_3$)	1677, 1697
6−PPh$_3$	1.35 (d, *J* = 2.0, 15 H)		7.45−7.62 (m, 15 H)	90.90 (d, *J* = 2.5)	8.23	164.69 (*C*O$_2$*C*O$_2$)	127.64 (d, *J* = 54.1) 128.63 (d, *J* = 10.5) 131.19 (d, *J* = 2.5) 134.18 (d, *J* = 10.6)	1677, 1694
6−NC$_5$H$_4$OMe[f]	1.54 (s, 15 H)		3.96 (s, 3 H) 6.90−6.98 (m, 2 H) 7.77 (t, *J* = 7.0, 1 H) 8.18 (d, *J* = 5.6, 1 H)	83.60	8.72	166.30 (*C*O$_2$*C*O$_2$)	57.55 (*C*H$_3$O) 108.41 (C-3) 118.66 (C-5) 142.53 (C-4) 149.97 (C-6) 164.04 (C-2)	1677, 1697
6−CO	1.88 (s, 15 H)			99.16	8.95	164.31 (*C*O$_2$*C*O$_2$)	168.50 (*C*O)	1673[d] 1707[d] 2064[d]

[a] $CDCl_3$ solvent, chemical shifts δ relative to those of C*H*Cl_3 = (7.27 ppm) and *C*DCl_3 (77.00 ppm). Coupling constants *J* in hertz. ND = not determined. [b] NMR and IR data from refs 1 and 2 unless otherwise noted. [c] Poor solubility precluded observation of the ^{13}C{^{1}H} NMR spectrum. [d] In $CDCl_3$. [e] IR data in $CDCl_3$ from this work. [f] NC_5H_4OMe = 2-methoxypyridine. ^{13}C resonances assigned with the aid of GHMQC and GHMBC experiments.

Alternative Synthesis of 6−PMe$_3$. To a suspension of [(η^5-C_5Me_5)-IrCl(μ-Cl)]$_2$ (68.8 mg, 0.0863 mmol) in dry THF (2 mL) was added PMe_3 (25 μL, 1.4 equiv), whereupon the solid dissolved rapidly. After 5 min, the orange solution was concentrated on the vacuum line, leaving an orange solid: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.71 (d, J = 2 Hz, 15 H), 1.66 (d, J = 11.2 Hz, 9 H). In the glovebox, the residue was dissolved in CH_3CN (2 mL), and $Ag_2C_2O_4$ (62.2 mg, 0.205 mmol, 1.19 equiv) was added. The flask was covered with foil, the contents were stirred for 14 h before CH_2Cl_2 (2 mL) was added outside the glovebox, and the now-yellow solution and white powder were filtered through a plug of Celite in a pipet. The plug was rinsed with CH_2Cl_2 in small portions, and combined filtrates were concentrated by rotary evaporation. The yellow solid remaining exhibited the same spectral properties as those reported above. The solid was dissolved in CH_2Cl_2 (ca. 1 mL), and a layer of THF (2 mL) was carefully added. Yellow crystals of **6**−PMe_3 (78.6 mg, 93%) were isolated by pipetting off the supernatant and storage under high vacuum. NMR spectral properties matched those of the sample prepared from $(\mathbf{3})_n$ and the literature values.[8]

Alternative Synthesis of 6−PEt$_3$. In a manner similar to that used for the PMe_3 analogue, [(η^5-C_5Me_5)IrCl(μ-Cl)]$_2$ (52 mg) and PEt_3 (0.02 mL) were combined in THF (5 mL); after isolation, the resulting intermediate was stirred in THF with $Ag_2C_2O_4$ (38.1 mg). The mixture was worked up as in the synthesis of **6**−PMe_3 and the crude product crystallized from CH_2Cl_2−hexanes to give yellow crystals of **6**−PEt_3 (54.9 mg, 55%).

Alternative Synthesis of 6−PPh$_3$. In a manner similar to that used for the PMe_3 analogue, [(η^5-C_5Me_5)IrCl(μ-Cl)]$_2$ (50.0 mg, 0.0628 mmol) and PPh_3 (32.9 mg, 0.126 mmol) were combined in CH_2Cl_2 (5 mL); after 1 d, to the resulting solution was added $Ag_2C_2O_4$ (38.2 mg, 0.126 mmol). After the mixture was stirred for 1 d, ^{1}H NMR spectral analysis of an aliquot revealed unreacted dichloro complex, so more $Ag_2C_2O_4$ (38.0 mg) was added and the mixture stirred for an additional 1 d before workup and crystallization gave yellow crystals of **6**−PPh_3 (47.5 mg, 53%).

Thermochemistry. General Considerations. All manipulations involving organoiridium complexes were performed under argon using standard high-vacuum or Schlenk tube techniques, or in a MBraun glovebox containing less than 1 ppm oxygen and water. Trimethylphosphine was purchased from Aldrich and used as received. Solvents were dried and distilled under argon before use employing standard drying agents.[9] Only materials of high purity as indicated by NMR spectroscopy were used in the calorimetric experiments. NMR spectra were recorded using a Varian Gemini 300 MHz spectrometer. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80) which was periodically calibrated using the TRIS reaction[10] or the enthalpy of solution of KCl in water.[11] The experimental enthalpies for these two standard reactions compared very closely to literature values. This calorimeter has been previously described,[12] and typical procedures are described below. Experimental enthalpy data are reported with 95% confidence limits.

NMR Titrations. Prior to every set of calorimetric experiments involving PMe_3, an accurately weighed amount (±0.1 mg) of the organoiridium complex was placed in a Wilmad screw-capped NMR tube and THF-d_8 was subsequently added. The solution was titrated with a solution of PMe_3 by injecting the latter in aliquots through the septum with a microsyringe, followed by vigorous shaking. The reactions were monitored by ^{31}P and ^{1}H NMR spectroscopy, and the reactions were found to be rapid, clean, and quantitative. These conditions are necessary for accurate and meaningful calorimetric results and were satisfied for all organometallic reactions investigated.

Solution Calorimetry. Calorimetric Measurement of Reaction between 2 and PMe$_3$. The mixing vessels of the Setaram C-80 were cleaned, dried in an oven maintained at 120 °C, and then taken into the glovebox. A 20 mg sample of **2** was accurately weighed into the lower vessel, which was closed and sealed with 1.5 mL of mercury. A 4 mL sample of a stock solution of PMe_3 (250 mg of PMe_3 in 20 mL of THF) was added, and the remainder of the cell was assembled, removed from the glovebox, and inserted into the calorimeter. The reference vessel was loaded in an identical fashion with the exception that no organoiridium complex was added to the lower vessel. After the calorimeter had reached thermal equilibrium at 30.0 °C (about 2 h), the calorimeter was inverted, thereby allowing the reactants to mix. After the reaction had reached completion and the calorimeter had once again reached thermal equilibrium (ca. 2 h), the vessels were removed from the calorimeter. Conversion to **5**−PMe_3 was found to be quantitative under these reaction conditions. Control reactions with Hg and PMe_3 showed no reaction. Enthalpy data are the average of five individual calorimetric determinations. The final enthalpy value (−28.5 ± 0.4 kcal/mol) represents the enthalpy of reaction with all species in solution. This methodology represents a typical procedure involving all organoiridium compounds and all reactions investigated in the present study.

Table 2. Crystallographic Data for **7**

empirical formula	$C_{22}H_{30}Cl_2Ir_2O_4$
fw	813.8
space group	$P2_1/c$
unit cell dimens	a = 8.205(2) Å
	b = 8.945(4) Å
	c = 16.714(6) Å
	β = 94.22(2)°
V (Å^3)	1223.3(10)
Z	2
temp (°C)	−100
radiation	Mo Kα (λ = 0.710 73 Å)
density (calcd)	2.209
abs coeff (mm^{-1})	11.072
quantity minimized	$\sum w(F_o - F_c)^2$
final R indices[a] (obsd data)	$R1$ = 2.31%, w$R2$ = 3.36%
R indices (all data)	$R1$ = 3.49%, w$R2$ = 3.93%

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. w$R2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. GOF = $[\sum[w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$, where n = number of reflections and p = number of parameters refined. $w = 1/[\sigma^2(F_o^2) + (0.0326P)^2 + 224.2319P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Enthalpy of Solution of 2. To consider all species in solution, the enthalpy of solution of **2** had to be directly measured. This was performed by using a procedure similar to the one described above with the exception that no PMe_3 was added to the reaction cell. The enthalpy of solution, 4.1 ± 0.2 kcal/mol, represents the average of five individual determinations.

Crystal Structure of 7. A yellow crystal of suitable size was mounted vertically in a 0.3 mm X-ray capillary and centered optically on a Siemens P4 autodiffractometer, precooled to −100 °C with the LT-2a low-temperature device. The centering of 25 randomly chosen reflections with 15° ≥ 2θ ≥ 30° led to the selection of a primitive monoclinic cell. Data were collected at −100 °C (Table 2). The space group was chosen on the basis of the systematic absences (0k0, k odd; h0l, l odd). The structure was solved using Patterson methods, and refinement of the non-hydrogen atoms to convergence was carried out using the SHELXTL Plus package of programs from Siemens (Madison, WI). Hydrogen atoms were generated in idealized positions with fixed isotropic thermal parameters. The asymmetric unit represents half of the centrosymmetric dinuclear complex that is generated through the inversion center of the molecule. An empirical absorption correction using the ψ scan data was attempted, but no improvement in the refinement or in the minimization of the peaks in the vicinity of the Ir atom could be attained. See Table 3 for the most important bond lengths and angles.

Results and Discussion

Syntheses and Ligand Additions. η^2-(*N*,*N*)-Bis(sulfonamido) chelate complex **1** was prepared in much the same way as **2**:[1,2] $TsNHCH_2CH_2NHTs$[6] reacted with solid K_2CO_3 and 0.5 mol of

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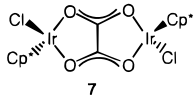
Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for **7**

Ir−Cl	2.381(2)	Cl−Ir−O(1)	85.5(2)
Ir−O(1)	2.145(5)	Cl−Ir−O(2)	85.0(2)
Ir−O(2)	2.157(5)	O(1)−Ir−O(2)	76.9(2)
O(1)−C(6)	1.255(9)	O(1)−C(6)−C(6a)	116.7(8)
O(2)−C(6a)	1.250(9)	O(1)−C(6)−O(2a)	125.3(7)
Ir−C(1)	2.115(7)	C(6a)−C(6)−O(2a)	118.0(8)
Ir−C(2)	2.121(7)	Ir−O(1)−C(6)	114.3(4)
Ir−C(3)	2.123(7)	Ir−O(2)−C(6a)	113.5(5)
Ir−C(4)	2.117(7)		
Ir−C(5)	2.131(8)		

the dimer $[(\eta^5\text{-}C_5Me_5)IrCl(\mu\text{-}Cl)]_2$[7] in CH_2Cl_2 to form **1** as a deep burgundy solid in 98% yield. The ^{1}H NMR spectroscopic data for **1** in $CDCl_3$ revealed a singlet at δ 2.76 ppm for all four methylene protons (Table 1), consistent with a monomeric structure like that of crystallographically characterized **2**, in which the C_5Me_5 centroid and the five atoms of the chelate ring lie nearly in the same plane.[1,2] When a dark red solution of **1** in $CDCl_3$ was treated with PMe_3, the color immediately changed to yellow, and ^{1}H NMR spectroscopy revealed two multiplets at 2.27 and 2.72 ppm, each integrating for two protons, changes expected to accompany formation of **4**−PMe_3 and its AA′MM′ spin system. Similar changes in ^{1}H NMR spectroscopic data and color occurred when **4**−CO was formed from **1** by bubbling CO through a $CDCl_3$ solution of **1** for about 2 min.

Installation of the oxalato ligand on $(\eta^5\text{-}C_5Me_5)Ir$ proved to be more problematic, requiring the use of silver oxalate[13] on the dimer $[(\eta^5\text{-}C_5Me_5)IrCl(\mu\text{-}Cl)]_2$. Even with use of excess silver oxalate, however, in reaction solvent CH_2Cl_2 or THF only half the chloride ligands were exchanged and yellow-orange crystals of oxalato-bridged dimer **7**, which is somewhat soluble

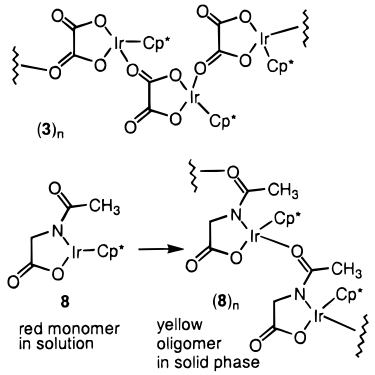


7

in CH_2Cl_2, were formed. The dimeric structure was suggested by the observation of a single very strong infrared absorption at 1620 cm^{-1}, similar to the spectral data for other $\mu\text{-}\eta^2\text{-}\eta^2\text{-}C_2O_4$ complexes[14,15] and different from the two bands seen between 1650 and 1750 cm^{-1} for most $\eta^2\text{-}C_2O_4$ complexes.[13−15] Furthermore, the combustion analyses for C and H were in accord with the proposed structure, although the calculated values for **7** and **3** were fairly close. An X-ray diffraction study on crystals grown from CH_2Cl_2−THF identified the structure of **7** (vide infra).

On the other hand, if CH_3CN was used as reaction solvent for silver oxalate and $[(\eta^5\text{-}C_5Me_5)IrCl(\mu\text{-}Cl)]_2$, after filtration and removal of solvent from the filtrate and recrystallization from CH_2Cl_2−THF, a yellow powdery solid giving correct combustion data for **3**·0.5 CH_2Cl_2 could be obtained in 78% yield. The yellow color of the product and its curiously low solubility in $CDCl_3$ strongly suggested that the compound was not the monomeric 16-electron structure represented by **3**, but rather was an oligomer or polymer in which each metal center achieved coordinative saturation as schematically illustrated in structure $(\mathbf{3})_n$ (Scheme 2). By comparison, 18-electron amino acid complexes **5** are all yellow solids, whereas their coordinatively unsaturated precursors **2** are red.[1,2] Furthermore, as adduced by comparison of IR spectra,[1,2] related complex **8** appears to exist as a red monomer in CH_2Cl_2 solution, but as a yellow oligomer or polymer, $(\mathbf{8})_n$, involving bridging by the amide group in the solid state. To gain more information about the structure of $(\mathbf{3})_n$, its ligand addition chemistry was explored.

Scheme 2



A suspension of presumed $(\mathbf{3})_n$ in $CDCl_3$ exhibited a weak singlet at δ 1.66 ppm from the small amount of dissolved compound. The yellow solid dissolved within 1 min when PMe_3 was added. In the ^{1}H NMR spectrum of the resulting yellow solution, doublets at δ 1.65 (J = 1.5 Hz, 15 H) and 1.45 (J = 11.2 Hz, 9 H) were consistent with the presence of the known[8] complex **6**−PMe_3, which was isolated in 75% yield. The same complex could also be made in 93% yield by initial addition of PMe_3 to $[(\eta^5\text{-}C_5Me_5)IrCl(\mu\text{-}Cl)]_2$ to form $(\eta^5\text{-}C_5Me_5)IrCl_2(PMe_3)$,[16] followed by reaction with $Ag_2C_2O_4$ in CH_3CN. In **6**−PMe_3 the presence of the oxalato ligand was confirmed by a singlet in the ^{13}C NMR spectrum at δ 165.63 ppm. However, the most striking spectroscopic differences between $(\mathbf{3})_n$ and **6**−PMe_3 appeared in IR spectra. Whereas the IR spectrum of **6**−PMe_3 in KBr showed two absorptions at 1677 and 1698 cm^{-1}, attributable to the symmetrical and asymmetrical stretching of the carbonyl groups,[13,14] the spectrum of $(\mathbf{3})_n$ in KBr showed four very strong absorptions at 1595, 1633, 1675, and 1699 cm^{-1}, which would be consistent with oxalato ligands in both bridging and terminal coordination modes in $(\mathbf{3})_n$. Therefore, comparison of the IR data for $(\mathbf{3})_n$ and **6** strongly suggests the conversion of bridging oxalato ligands in $(\mathbf{3})_n$ to a chelating one in **6**.

Oligomer $(\mathbf{3})_n$ appears to be a versatile precursor to other complexes. For example, **6**−PEt_3 and **6**−PPh_3 could be made in over 90% yield in one step from $(\mathbf{3})_n$ and the appropriate phosphine. Independent syntheses were accomplished from initial reaction of dimer $[(\eta^5\text{-}C_5Me_5)IrCl(\mu\text{-}Cl)]_2$ with the appropriate phosphine, followed by introduction of silver oxalate. The IR and NMR spectroscopic data for the two new phosphine complexes resembled those of **6**−PMe_3 (Table 1).

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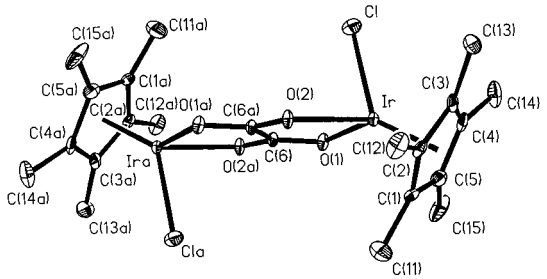

Figure 1. A view of the structure of complex **7**.

In addition, 2-methoxypyridine added readily to provide **6**−NC_5H_4OMe in 88% yield, and saturation of a suspension of $(\mathbf{3})_n$ in $CDCl_3$ with CO provided **6**−CO after 0.5 h.

Finally, upon addition of PMe_3, dimer **7** disproportionated to give a mixture of $(\eta^5\text{-}C_5Me_5)IrCl_2(PMe_3)$[16] and **6**−$PMe_3$.

Thermochemistry of Ligand Addition. The enthalpies of solution for **1** and **2** in THF were +5.0(0.3) and +4.1(0.2) kcal mol^{-1}, respectively. Enthalpies of reaction between PMe_3 and **1** and **2** were −23.7(0.5) and −24.4(0.3) kcal mol^{-1}, respectively. Therefore, the enthalpies of reaction with all species in solution amounted to −28.7(0.5) and −28.5(0.4) kcal mol^{-1} for **1** and **2**, the same within experimental uncertainty. Unfortunately, the analogous oxalato complex formulated as $(\mathbf{3})_n$ exhibited negligible solubility in THF and could not be used in these experiments. Very few systems of this kind have been studied, so given the limited data it is not clear why the enthalpy difference between two ligand additions is experimentally negligible.

Crystal Structure of 7. Yellow plates of **7** suitable for an X-ray diffraction study were obtained from CH_2Cl_2−THF. The structure (Figure 1) verifies the basic constitution of the molecule and is centrosymmetric, containing an inversion center. Many such structures are known,[15,17] and the one reported agrees well with the literature examples. For example, within experimental uncertainty, the bond lengths C(6)−O(1) and C(6a)−O(2) are identical [1.255(9) and 1.250(9) Å, respectively], and are the same as values reported for other $\mu\text{-}\eta^2\text{-}\eta^2\text{-}C_2O_4$ complexes.[15,17] In contrast, in mononuclear $\eta^2\text{-}C_2O_4$ oxalato complexes the average lengths of the C═O and C−O bonds are 1.224 and 1.279 Å, respectively.[18]

Comparisons of Carboxylato and *N*-Tosylamido Ligands. Color, solubility, and IR spectral data are key indicators of the structure of the complexes considered in this paper and, ultimately, of the behavior of ligands on the $(\eta^5\text{-}C_5Me_5)Ir^{III}$ fragment. We have previously shown that **2** is a red monomer in the solid state.[1,2] From the work described here, complexes **1** and **2**, which both have sulfonamido ligands, show very similar properties: both are red in color and formally 16-electron species, either in solution or in the solid state. In comparison, previous work[1,2] showed that related amidato complex **8** (Scheme 2) is red in solution but yellow in the solid state. Changes in IR absorptions pointed to oligomerization or polymerization in the solid state with concomitant formation of coordinatively saturated Ir centers in $(\mathbf{8})_n$.

In the present study, attempted formation of **3** led to isolation of a yellow, poorly soluble solid, formulated as an oligomer or polymer, $(\mathbf{3})_n$, which dissolves only on addition of a two-electron donor such as a phosphine, CO, or 2-methoxypyridine, forming yellow solutions of **6**. We noted that $(\mathbf{3})_n$ dissolved in CH_3CN, but on removal of solvent, only $(\mathbf{3})_n$ remained, free of CH_3CN. Similar behavior has been observed for $(\eta^5\text{-}C_5Me_5)Ru(proline)$.[19] Comparison of IR spectral data for $(\mathbf{3})_n$ and **6** strongly suggest the conversion of unsymmetrical bridging oxalato ligands to chelating ones. Although the insolubility of $(\mathbf{3})_n$ precluded extension of thermochemical studies to include the entire series **1**-**3**, we thought that the carboxylato ligand was smaller and a poorer donor than the *N*-tosylamido ligand, leading to the propensity for **3** to oligomerize. The importance of electronic properties is suggested by comparison of the acidities of bound water molecules in Ru complexes, which led other workers[15h] to conclude that an acetylacetonato ligand is a better π-donor than an oxalato ligand.

To determine the role of electronic factors, the CO adducts of **1**−**3** (**4**−CO, **5**−CO, and **6**−CO) were examined by IR spectroscopy in $CDCl_3$ solution.[20] Others have used ν_{CO} as a probe of the electron density of a metal center.[21] The observed values of ν_{CO} in **4**−CO (2042 cm^{-1}), **5**−CO (2049 cm^{-1}), and **6**−CO (2064 cm^{-1}) clearly indicate that the sulfonamido ligands are better donors than the oxalato ligand. Interestingly, the replacement of one sulfonamido group in **4**−CO with a carboxylato group results in a slight change (7 cm^{-1}), whereas replacement of the sole sulfonamido in **5**−CO with a carboxylato group produces a larger change (15 cm^{-1}). The π-donating abilities of sulfonamide and carboxylate substituents in organic compounds have been compared using variants of the Hammett equation.[22] Focusing on the effect of an aromatic substituent on the para position, which is taken as a measure of π-donation or -acceptance, it appears that the $-NHSO_2Ph$ group (σ_P = −0.01 or +0.01) is a better donor than the O_2CCH_3 substituent (σ_P = 0.31). However, in electronically saturated 18-electron metal centers such as those found in **4**−CO, **5**−CO, and **6**−CO, there is typically no significant π-interaction between the metal and oxo and amide ligands.[5] Therefore, although π-donation is important in formally 16-electron complexes **1**−**3**,[1,2] the differences in IR data for the three electronically saturated CO complexes may be ascribed to superior σ-donation of the sulfonamido ligand compared with that of the carboxylato ligand. Relevant literature examples of spectroscopic changes accompanying changes in pure σ-donating ability are (dien)-$Mo(CO)_3$ (1883 and 1723 cm^{-1})[23a] and the analogous permethylated complex of $Me_2NCH_2CH_2N(Me)CH_2CH_2NMe_2$ (1907, 1774, and 1755 cm^{-1}),[23b] or the $Mo(CO)_3$ complexes of 1,4,7-triazacyclononane (1850 and 1740−1700 cm^{-1})[24a] and a peralkylated analogue (1895, 1759, and 1729 cm^{-1}).[24b] Taken together with the large difference in structure between monomer **2**[1,2] (with one carboxylato ligand) and oligomer $(\mathbf{3})_n$ (with two carboxylato ligands per monomer), we conclude that one sulfonamido group provides sufficient donation, whether in σ- or π-fashion, to stabilize the monomeric form.

Finally, we note that the removal of all chloride ligands from

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$[(\eta^5\text{-}C_5Me_5)IrCl(\mu\text{-}Cl)]_2$ in the synthesis of oxalato complex $(\mathbf{3})_n$ required the use of silver ion and the polar, coordinating solvent CH_3CN, whereas synthesis of chelate complexes **1** and **2** could be accomplished using only potassium carbonate, even in dichloromethane, perhaps a reflection of the relative nucleophilicities of the conjugate bases of oxalic acid and *N*-sulfonamides.

Conclusions

The characterization of monomers **1** and **2** and oligomer or polymer $(\mathbf{3})_n$ and IR spectroscopic data on the corresponding CO adducts point to the competence of the *N*-tosylamido ligand as a π- or σ-donor, which has bearing on the application of the sulfonamido ligands to catalysis.[4] Furthermore, $(\mathbf{3})_n$ is a versatile precursor to monomeric complexes **6** by simple ligand addition.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure of **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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