Oxidative Addition Reactions of the Bridging Amido Complex Ir$_2$[μ-NH(p-tolyl)]$_2$(CO)$_4$: X-ray Crystal Structure of the 16e–18e Dimer Ir$_2$(Me)(I)[μ-NH(p-tolyl)]$_2$(CO)$_4$·0.25C$_6$H$_{14}$

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Oxidative addition reactions of halogens, hydrogen chloride, and methyl iodide with the dinuclear bridging amido complex Ir$_2$[μ-NH(p-tolyl)]$_2$(CO)$_4$ are described. For Cl$_2$, Br$_2$, MeI, and HCl, addition of 1 equiv produces Ir(I)–Ir(III) dimers, whereas 1 equiv of I$_2$ produces an Ir(II)–Ir(II) dimer. Except for the MeI addition reaction, all of the oxidative addition processes proceed to give Ir(III)–Ir(III) dimers as final products. The characterization of the MeI addition product was performed by an X-ray analysis, showing two iridium centers, with pseudooctahedral and pseudo-square-planar environments, that are separated by 3.209(1) Å. Crystal data: C$_{19}$H$_{19}$-IIr$_2$N$_2$O$_4$·0.25C$_6$H$_{14}$; triclinic P$\bar{1}$, a = 12.568(3) Å, b = 12.801(3) Å, c = 17.248(3) Å, α = 69.82(3)°, β = 85.45(3)°, γ = 74.12(3)°, V = 2504.8(9) Å^3, Z = 4, $R(F)$ = 0.046, and $R(wF)$ = 0.054 for 5389 (F > 5σ(F)) reflections.

Introduction

Simple alkyl- and arylamido groups (NHR$^-$ or NH$_2^-$) are important in transition metal chemistry due to their variable σ/π donor ability and their reactive nature. The nucleophilic nature of the metal–amide bond can promote addition reactions across unsaturated organic functional groups. The chemistry of transition metal–amido complexes has been studied mainly for early transition metals in high oxidation states,[1] in which the amido nitrogen is usually found to be unreactive due to ligand-to-metal π bonding. Since late transition metals in their lower oxidation states resist any substantial π bonding from coordinated ligands, there has been a recent surge in interest in the chemistry of late transition metal-amido complexes.[2–5] Although a number of studies have been published recently for the metals Ru(II),[5] Ir(III),[3a–d] Pd-(II),[4] and Pt(II)[4], there has been no systematic study reported for simple alkyl- or arylamido complexes of rhodium and iridium in their +1 oxidation state. We have

initiated a study to prepare and characterize such complexes, employing π-accepting ancillary ligands to provide greater stability to the metal–amido bond. The preparations of the dinuclear complex M$_2$(μ-NHAr)$_2$(CO)$_4$ [M = Rh and Ir, Ar = Ph, p-tolyl],[6] and the mononuclear complex Ir(CO)(NHAr)(PPh$_3$)$_2$ [Ar = Ph,p-tolyl, 2,6-C$_6$H$_3$-Me$_2$],[7] II, have been accomplished to date, and schematic representations of their structures are shown.
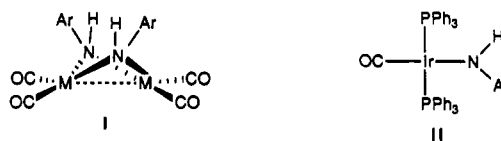
Structurally, the Ir–p-toluidide analog of I is similar to the pyrazolyl bridged diiridium tetracarbonyl complexes that have been studied extensively by Stobart *et al.*[8] An X-ray crystal structure of the p-toluidide complex shows the presence of a short, 2.933(1) Å, metal–metal distance in the molecule. To our knowledge, this distance is among one of the shortest observed thus far for structurally similar complexes containing a thiolato, pyrazolyl, phosphido, or a naphthalenediamido group as the bridging ligand.[9]

Several studies aimed at elucidating the reactivity of I are underway in our laboratory and will be reported in the future. This paper describes the initial results of oxidative addition reactions of I with halogens, hydrogen chloride,

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and methyl iodide. Oxidative additions of substrates, being fundamentally important in many catalytic reactions, have been widely studied on mononuclear metal centers.[10] Similar studies on dinuclear metal centers still continue to be of interest.[11] In many cases, cooperative electronic and/or steric effects between two proximal reactive metal centers result in different reactivity patterns than those of the mononuclear cases. A critical consideration in studies involving dinuclear complexes is the rigidity of any bridging group present, the lack of which has provided misleading results.[11k] The observed rigidity of the bridging amido groups and the short intermetallic distance in the iridium analog of **I** prompted us to examine its oxidative addition reactions. We observe two two-electron oxidative addition steps that occur in a stepwise manner. Depending on the substrate, the first step in the addition process occurs at either one or both metal centers.

Experimental Section

All preparations were carried out under N_2 using standard drybox or Schlenk line techniques. Solvents were purified before use and stored under N_2 over 4-Å molecular sieves. Hexanes were distilled from CaH_2, methylene chloride was distilled from P_4O_{10}, and toluene and THF were distilled from Na/K alloy and benzophenone. NaOPh was prepared by the reaction of phenol with Na in THF and was recrystallized from THF. *p*-Toluidine and iodine were purified by sublimation before use. Chlorine and HCl gases were purchased from Matheson and were used without any further purification. Methyl iodide and bromine were purchased from Aldrich and were degassed before use. *cis*-Ir(CO)$_2$Cl(NH$_2$-*p*-tolyl) was synthesized according to a published method.[12]

Infrared spectra were obtained on a Nicolet 7000 series FT-IR instrument. ^1H and ^{13}C NMR spectra were recorded using a 250-, 270-, or 500-MHz Bruker instrument. Deuterated solvents for NMR experiments were purchased from Cambridge Isotope Laboratories. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, and Quantitative Technologies Inc., Whitehouse, NJ.

Syntheses. Ir$_2$(μ-NH(*p*-tolyl))$_2$(CO)$_4$ (1). To a 50-mL THF solution of *cis*-Ir(CO)$_2$Cl(*p*-toluidine) (2.0 g, 5.1 mmol) was added 1 equiv of NaOPh (0.59 g, 5.1 mmol) dissolved in 25 mL of THF. (A secondary reaction product becomes apparent when excess NaOPh is used, and the yield of **1** becomes lower.) The THF solution was stirred for approximately 10 min, at the end of which a complete disappearance of the ν(CO) bands associated with the starting complex was observed. At this point, the reaction

mixture was evacuated to dryness to afford a dark brown solid. The solid was extracted with 35 mL of toluene, filtered through a 0.5-in. pad of Celite, and reduced in volume to approximately 5 mL. Hexane (10 mL) was added to the toluene solution, and the mixture was cooled at -15 °C for 2 days to precipitate a mixture of yellow and purple crystals. The supernatant was syringed off, the crystals were washed with hexane, and the washing was added to the supernatant. Further reduction in volume and cooling of the supernatant produced a second batch of yellow and purple crystals. Combined yield: 1.7 g, 90%. IR (carbonyl region) (CH$_2$Cl$_2$, cm^{-1}): 2072 (w), 2051 (vs), 1991 (vs). ^1H NMR (CDCl$_3$) (chemical shifts are relative to TMS at δ 0): δ 7.05 (s, 4H, C$_6$*H*$_4$Me), 3.40 (br s, 1H, *H*N–), 2.33 (s, 3H, C$_6$H$_4$*Me*). ^{13}C NMR (CDCl$_3$) (chemical shifts are relative to CDCl$_3$ resonance at δ 77.0): δ 172.81 (s, *CO*), 153.39, 133.70, 129.17, 120.63 (s, *C*$_6$H$_4$-Me), 20.63 (s, C$_6$H$_4$*Me*). Anal. Calcd: C, 30.50; H, 2.28; N, 3.95. Found: C, 30.44; H, 2.33; N, 3.91.

Ir$_2$(Me)(I)[μ-NH(*p*-tolyl)]$_2$(CO)$_4$·0.25C$_6$H$_{14}$ (2). 1 (0.15 g, 0.21 mmol) was dissolved in 100 mL of toluene in a Schlenk flask under N_2 and a 1000-fold excess of MeI (13 mL, 29.8 g) was added in the dark. The solution was allowed to stir for 1.5 h, after which time it was evacuated to dryness. The dark green solid was extracted with hexane (20 mL) and filtered out and the filtrate was reduced in volume. Cooling to -15 °C afforded pale yellow crystals, yield 0.13 g, 60%. IR (carbonyl region) (hexane, cm^{-1}): 2113 (m), 2069 (s), 2063 (m), 1997 (s). ^1H NMR (CDCl$_3$): δ 7.20 (d) and 7.10 (d) (4H, C$_6$*H*$_4$Me), 5.07 (br s, 1H, *H*N–), 2.33 (s, 3H, C$_6$H$_4$*Me*), 2.00 (s, 1.5H, *Me*). ^{13}C NMR (CDCl$_3$): δ 172.81, 159.50 (s, *CO*), 151.49, 134.98, 129.29, 122.42 (s, *C*$_6$H$_4$Me), 20.69 (s, C$_6$H$_4$*Me*), -4.04 (s, *Me*). Anal. Calcd: C, 28.23; H, 2.60; N, 3.21. Found: C, 28.43; H, 2.41; N, 3.23.

Ir$_2$Cl$_2$[μ-NH(*p*-tolyl)]$_2$(CO)$_4$ (3a). To a toluene (75 mL) solution of 1 (0.10 g, 0.14 mmol) at 0 °C was added 1 equiv of Cl$_2$ gas (3.20 mL at 760 Torr, 0.14 mmol) via a gastight syringe. The initial yellow-brown solution gradually turned dark green within approximately 15 min, after which time the solution was concentrated to about 5 mL and hexane (15 mL) was added to precipitate a green microcrystalline product. Yield: 0.08 g, 75%. IR (carbonyl region) (CH$_2$Cl$_2$, cm^{-1}): 2142 (m), 2097 (m), 2068 (s), 1992 (s). ^1H NMR (CDCl$_3$): δ 7.47 (br) and 7.11 (d) (4H, C$_6$*H*$_4$Me), 4.83 (br s, 1H, *H*N–), 2.34 (s, 3H, C$_6$H$_4$*Me*). ^{13}C NMR (CDCl$_3$): δ 151.8 (s, *CO*), 151.47, 135.76, 129.48, 122.39 (s, *C*$_6$H$_4$-Me), 20.79 (s, C$_6$H$_4$*Me*). Anal. Calcd: C, 27.73; H, 2.07; N, 3.59. Found: C, 28.65; H, 2.31; N, 3.26.

Ir$_2$Br$_2$[μ-NH(*p*-tolyl)]$_2$(CO)$_4$ (3b). To 1 (0.10 g, 0.14 mmol), dissolved in 75 mL of toluene, was added 1 equiv of Br$_2$ (7.0 × 10^{-3} mL, 0.14 mmol) as a solution in toluene. The initial yellow-brown solution gradually turned purple in 10 min, after which time the solution was reduced in volume to about 5 mL and 15 mL of hexane was added to precipitate a green solid. The IR spectrum of the solid indicated the presence of **3b** along with a slight amount of **1**, which has been a persistent contaminant in this preparation. Attempts to fully convert **1** to **3b** by adding a slight excess of Br$_2$ always resulted in the formation of a significant amount of **4b** (*vide infra*). Hence, elemental analysis of **3b** was not performed. IR (carbonyl region) (CH$_2$Cl$_2$, cm^{-1}): 2124 (m), 2074 (m), 2067 (s), 1991 (s). ^1H NMR (CDCl$_3$): δ 7.50 (br) and 7.12 (d) (4H, C$_6$*H*$_4$Me), 5.29 (br s, 1H, *H*N–), 2.35 (s, 3H, C$_6$H$_4$*Me*).

Ir$_2$I$_2$[μ-NH(*p*-tolyl)]$_2$(CO)$_4$ (3c). A 0.10-g sample of 1 (0.14 mmol) was dissolved in toluene (25 mL) in a Schlenk flask. Then 1 equiv of I$_2$ (0.04 g, 0.14 mmol), dissolved in 15 mL of toluene, was added dropwise to the above solution, causing a gradual color change of the solution from yellowish brown to green to finally reddish brown. After the addition was complete, the solution was concentrated under reduced pressure and hexane

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Table I. Crystallographic Data for 2

formula	$C_{19}H_{19}IIr_2N_2O_4\cdot0.25C_6H_{14}$
fw	870.25
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	12.568(3)
b, Å	12.801(3)
c, Å	17.248(3)
α, deg	69.82(3)
β, deg	85.45(3)
γ, deg	74.12(3)
V, Å³	2504.8(9)
Z	4
μ(Mo Kα), cm⁻¹	118.21
D(calc), g cm⁻³	2.315
$R(F)$, %	4.60
$R(wF)$,^{a} %	5.37
δ/σ (max)	0.016
GOF	1.10

^{a} $w^{-1} = \sigma^2(F) + 0.001(F)^2$.

was added to precipitate a reddish brown microcrystalline solid. Yield: 0.13 g, 95%. IR (carbonyl region) (CH₂Cl₂, cm⁻¹): 2103 (vs), 2082 (s), 2047 (s). ¹H NMR (CDCl₃): δ 7.08 and 7.04 (4H, C₆H₄Me), 5.35 (br s, 1H, HN–), 2.29 (s, 3H, C₆H₄Me). ¹³C NMR (CDCl₃): δ 167.02 (s, CO), 148.73, 136.62, 129.87, 122.53 (s, C₆H₄-Me), 20.76 (s, C₆H₄Me). Anal. Calcd: C, 22.53; H, 1.68; N, 2.92. Found: C, 22.39; H, 1.69; N, 2.75.

Ir₂Cl₄[μ-NH(p-tolyl)]₂(CO)₄ (4a). Cl₂ gas was bubbled through a 25-mL toluene solution of 1 (0.10 g, 0.14 mmol) at room temperature for ~5 min. The initial yellowish brown solution turned bright yellow, from which a yellow microcrystalline solid was obtained by adding hexanes. Yield: ~90%. IR (carbonyl region) (CH₂Cl₂, cm⁻¹): 2148 (vs), 2108 (vs). ¹H NMR (CDCl₃): δ 7.79 (br) and 7.14 (d) (4H, C₆H₄Me), 6.10 (br s, 1H, HN–), 2.36 (s, 3H, C₆H₄Me). The ¹³C NMR spectrum of this complex was not recorded. Anal. Calcd: C, 25.42; H, 1.90; N, 3.29. Found: C, 25.67; H, 1.91; N, 2.76.

Ir₂Br₄[μ-NH(p-tolyl)]₂(CO)₄ (4b). To 1 (0.10 g, 0.14 mmol) in 25 mL of toluene was added 2 equiv of Br₂ (0.045 g, 0.28 mmol). The mixture was allowed to react for 5 min, after which time the volume of the solution was reduced to 5 mL and 15 mL of hexane was added to precipitate a bright yellow solid. Yield: ~89%. IR (carbonyl region) (CH₂Cl₂, cm⁻¹): 2144 (s), 2103 (s). ¹H NMR (CDCl₃): δ 7.79 (br) and 7.14 (d) (4H, C₆H₄Me), 6.37 (br s, 1H, HN–), 2.36 (s, 3H, C₆H₄Me). The ¹³C NMR spectrum was not recorded. Anal. Calcd: C, 21.02; H, 1.57; N, 2.72. Found: C, 21.20; H, 1.45; N, 2.66.

Ir₂I₄[μ-NH(p-tolyl)]₂(CO)₄ (4c). To a 25-mL toluene solution of 1 (0.10 g, 0.14 mmol) was added 2 equiv of I₂ (0.07 g, 0.28 mmol). The reaction was found to reach its completion in 10 min. The workup procedure was as described for 4b. Yield: ~95%. IR (carbonyl region) (CH₂Cl₂, cm⁻¹): 2132 (s), 2093 (s). ¹H NMR (CDCl₃): δ 7.81 (br) and 7.14 (d) (4H, C₆H₄Me), 6.64 (br s, 1H, HN–), 2.36 (s, 3H, C₆H₄Me). ¹³C NMR (CDCl₃): δ 150.91 (s, CO), 150.44, 136.45, 129.43, 121.99 (s, C₆H₄Me), 20.75 (s, C₆H₄Me). Anal. Calcd: C, 17.77; H, 1.33; N, 2.30. Found: C, 18.24; H, 1.39; N, 1.98.

Ir₂(H)(Cl)[μ-NH(p-tolyl)]₂(CO)₄ (5). To a 25-mL toluene solution of 1 (0.10 g, 0.14 mmol) was added 1 equiv of HCl gas (3.5 mL at 760 Torr, 0.14 mmol) via a gastight syringe. The solution of the parent compound turned pale pink, and the reaction was complete in ~40 min. The product was isolated as a green solid, contaminated by a slight amount of 1. Yield: ~75%. IR (carbonyl region) (CH₂Cl₂, cm⁻¹): 2127 (m), 2067 (s), 1992 (s). ¹H NMR (CDCl₃): δ 7.17 (d) and 7.11 (d) (4H, C₆H₄Me), 4.28 (br, s, 1H, HN–), 2.32 (s, 3H, C₆H₄Me), –12.63 (s, 0.5H, Ir–H).

Ir₂(H)₂(Cl)₂[μ-NH(p-tolyl)]₂(CO)₄ (6). To a 25-mL toluene solution of 1 (0.10 g, 0.14 mmol) was added 2 equiv of HCl gas (7.0 mL at 760 Torr, 0.28 mmol) via a gastight syringe. The mixture was allowed to react for 20 min. The final workup yielding the product was similar to that described for 4b. Yield:

Table II. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) for the Two Crystallographically Independent Molecules of 2

	x	y	z	U(eq)^a
Ir(1)	10148(1)	1562(1)	7093(1)	38(1)
Ir(2)	8254(1)	3940(1)	6750(1)	39(1)
I	8927(1)	–41(1)	7637(1)	56(1)
N(1)	9094(10)	2539(10)	7759(8)	39(5)
N(2)	8842(10)	2612(9)	6251(7)	32(5)
O(1)	11836(14)	154(12)	8474(9)	101(8)
O(2)	11397(12)	333(12)	5962(9)	77(7)
O(4)	7446(14)	5598(12)	7661(9)	89(8)
O(5)	7202(12)	5820(12)	5227(9)	84(7)
C(1)	11178(16)	687(14)	7973(11)	52(8)
C(2)	10950(15)	762(15)	6397(11)	50(8)
C(3)	11013(14)	2855(13)	6647(10)	48(7)
C(4)	7765(16)	4961(15)	7309(11)	59(9)
C(5)	7582(15)	5072(15)	5815(12)	53(8)
C(11)	10057(16)	3613(14)	8299(12)	56(8)
C(12)	10520(16)	3730(16)	8955(13)	65(10)
C(13)	10523(18)	2962(18)	9742(12)	72(10)
C(14)	10097(21)	2070(17)	9842(12)	78(11)
C(15)	9603(15)	1940(13)	9223(11)	51(8)
C(16)	9567(14)	2738(12)	8419(9)	39(7)
C(17)	11093(24)	3123(23)	10415(15)	142(18)
C(21)	9586(12)	3627(12)	4886(10)	40(7)
C(22)	9814(14)	3724(15)	4071(10)	50(8)
C(23)	9575(18)	3066(16)	3693(12)	61(9)
C(24)	9013(19)	2272(17)	4164(12)	73(11)
C(25)	8772(16)	2148(14)	5002(11)	55(9)
C(26)	9062(13)	2824(13)	5365(9)	39(7)
C(27)	9828(21)	3212(18)	2820(12)	90(12)
Ir(1')	4522(1)	2627(1)	7153(1)	40(1)
Ir(2')	6309(1)	2179(1)	8542(1)	38(1)
I'	5834(1)	2916(1)	5765(1)	58(1)
N(1')	5893(10)	1315(10)	7816(8)	37(5)
N(2')	5406(10)	3554(10)	7552(7)	36(5)
O(1')	3526(12)	1023(12)	6707(9)	77(8)
O(2')	2725(12)	4755(12)	6291(9)	87(7)
O(4')	7526(12)	85(12)	9852(8)	78(7)
O(5')	6848(13)	3565(12)	9463(9)	82(8)
C(1')	3903(15)	1648(18)	6845(13)	63(10)
C(2')	3376(15)	3958(16)	6604(10)	51(8)
C(3')	3568(14)	2395(14)	8245(10)	50(8)
C(4')	7054(14)	889(16)	9345(10)	47(8)
C(5')	6630(14)	3078(15)	9096(11)	50(8)
C(11')	6176(13)	–620(13)	7723(10)	43(7)
C(12')	6141(15)	–1737(14)	8037(11)	54(8)
C(13')	5714(16)	–2182(14)	8849(11)	55(8)
C(14')	5375(14)	–1423(15)	9254(11)	51(8)
C(15')	5393(15)	–312(14)	8958(10)	51(8)
C(16')	5802(12)	142(12)	8154(10)	37(6)
C(17')	5715(20)	–3422(14)	9200(12)	82(11)
C(21')	4219(18)	4699(15)	8358(12)	69(10)
C(22')	3600(19)	5746(18)	8387(15)	86(12)
C(23')	3532(19)	6770(17)	7750(18)	88(13)
C(24')	4105(21)	6686(19)	7022(17)	90(13)
C(25')	4730(16)	5641(16)	6958(12)	65(9)
C(26')	4792(14)	4635(13)	7636(10)	46(7)
C(27')	2849(25)	7892(18)	7847(18)	150(20)
C(100)	3922(43)	1226(42)	4496(29)	233(21)
C(101)	4388(27)	160(33)	4855(23)	157(13)
C(102)^b	2631(29)	1521(27)	4192(20)	139(11)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor. ^{b} Note: Atoms C(100) to C(102) are for the disordered molecule of hexane.

~90%. IR (carbonyl and hydride region) (CH₂Cl₂, cm⁻¹): 2183 (br w, Ir–H), 2126 (s), 2079 (s). ¹H NMR (CDCl₃): δ 7.58 (br) and 7.06 (d) (4H, C₆H₄Me), 4.84 (br s, 1H, HN–), 2.34 (s, 3H, C₆H₄Me), –11.79 (s, 1H, Ir–H).

X-ray Structural Analysis of Ir₂(Me)(I)[μ-NH(p-tolyl)]₂-(CO)₄·0.25C₆H₁₄. Crystallographic data are collected in Table I, and atomic coordinates are given in Table II. Photographic data revealed no symmetry higher than triclinic, and the
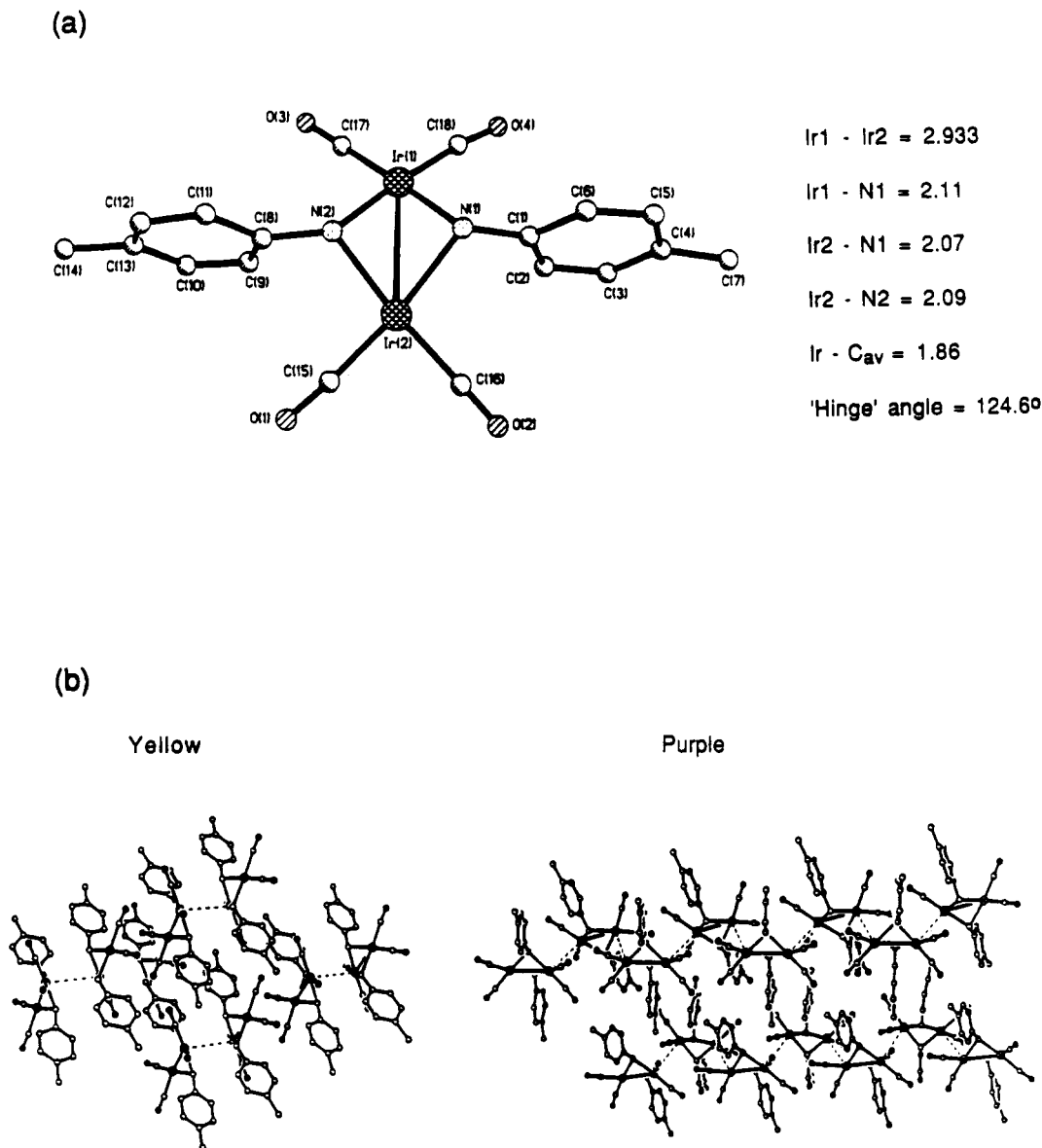
(a)

Ir1 - Ir2 = 2.933

Ir1 - N1 = 2.11

Ir2 - N1 = 2.07

Ir2 - N2 = 2.09

Ir - C$_{av}$ = 1.86

'Hinge' angle = 124.6°

(b)

Yellow

Purple

Figure 1. (a) Ball and stick diagram of 1. (b) Packing of molecules in the two crystalline modifications of 1.

centrosymmetric space group $P\bar{1}$ was initially selected on the basis of its frequency of occurrence. The results of refinement support this choice. Correction for absorption was applied to the diffraction data by empirical methods. Following anisotropic refinement of all non-hydrogen atoms, a partially disordered molecule of hexane was located on an inversion center resulting in an asymmetric unit consisting of two crystallographically independent molecules and the half molecule of solvent. All computations used SHELXTL-PC software (G. Sheldrick, Siemens, Madison, WI).

Results

Synthesis of Ir$_2$(μ-NH(p-tolyl))$_2$(CO)$_4$, 1. A brief description of the syntheses of the Rh and Ir dimers has been published earlier.[6] The formation of the complexes can be best achieved by the addition of NaOPh to *cis*-M(CO)$_2$Cl(NH$_2$R), where R = a phenyl or a substituted phenyl group.

$$2cis\text{-M(CO)}_2\text{Cl(NH}_2\text{R)} + 2\text{NaOPh} \rightarrow$$
$$\text{M}_2\text{(CO)}_4(\mu\text{-NHR})_2 + 2\text{NaCl} + 2\text{PhOH}$$
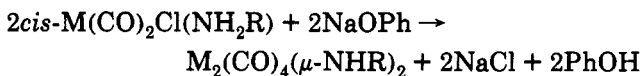
In a typical preparative scale reaction, 1.0 g of the amine complex is reacted with sodium phenoxide to give the

product in ~90% yield. Recrystallization of the crude product from a toluene/hexane mixture produces crystals of two different colors, which were determined to be polymorphs of 1 by X-ray crystallography. The molecular geometry of the dimer is virtually identical in the two crystalline forms, exhibiting two square-planar iridium centers bridged by two p-tolylamido groups (Figure 1a). In the yellow form (triclinic), the two Ir centers are separated by 2.933(1) Å. The distance is slightly longer, 2.968(2) Å, in the purple form (orthorhombic) of crystals. Although both the metal centers are d^8, these distances are extremely short and can be considered as single bond distances. As shown in the packing diagrams of Figure 1b, the dimer molecules in yellow crystals make short intermolecular contact in a pairwise fashion, the Ir···Ir contact being 3.98 Å. In the purple crystals, intermolecular contacts extend over an infinite linear array with a much shorter Ir···Ir contact, 3.75 Å. Thus, the long chain of metal–metal contacts in the latter case probably gives rise to its dark color.

Though vastly different in color in the solid state, the two polymorphs of 1 produce identically colored solutions and show three ν(CO) bands (CH$_2$Cl$_2$) at 2072 (m), 2051
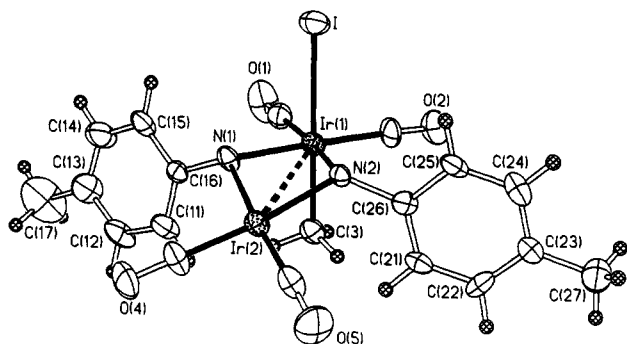
Figure 2. ORTEP view of **2** with 40% probability thermal ellipsoids.

(vs), and 1991 (vs) cm^{-1}, indicating loss of extended metal–metal contact but preservation of the bent structure (C_{2v}) in solution. The room temperature ^{1}H NMR spectrum in CDCl$_3$ shows a single resonance for the Me substituent of the tolyl group (δ 2.33) and also for the –NH– group (δ 3.40) of the bridging amido moiety, indicating either the presence of a single isomer or a rapid exchange between two or more isomers in solution. To examine the latter possibility, a variable temperature ^{1}H NMR study of **1** was carried out in C$_6$D$_5$CD$_3$ between –63 and +77 °C. The number of Me and –NH– resonances remained unchanged in this temperature range, except for small changes in their chemical shifts due to changes in temperature. This result clearly shows that, in solution, **1** only gives rise to a single isomer. Moreover, we have recorded the IR spectra of **1** in different solvents, e.g. CH$_2$Cl$_2$, hexane, and THF, and all of the spectra display only a three band pattern with identical intensity ratios. We find it rather interesting that the isomer where both of the tolyl groups are *cis* with respect to each other is formed selectively.

The phenyl protons of **1** appear as a singlet in CDCl$_3$, although the expected two doublet pattern is observed in C$_6$D$_6$ and C$_6$D$_5$CD$_3$. The ^{13}C NMR spectrum of **1** shows a set of four resonances for the carbon atoms of the *p*-tolyl moiety in the expected region of the spectrum. Also, only a single resonance is observed at δ 172.8 for the four CO ligands, consistent with the presence of a single isomer in solution.

Reaction with MeI. Complex **1** reacts in an oxidative addition fashion with excess MeI to produce Ir₂(Me)(I)-(μ-NH(p-tolyl))₂(CO)₄, **2**, as a pale yellow crystalline solid. The reaction is exceedingly slow and requires the addition of a 500–1000-fold excess of MeI. Analogous to the pyrazolyl-bridged iridium carbonyl dimer,[8] we had anticipated a two-center 2-electron oxidative addition reaction in this case. Instead, the addition was found to occur to *only one* metal center, resulting in an Ir(I)–Ir(III) or a 16e–18e dimer, as shown in Figure 2. IR and NMR data of complex **2** are consistent with the solid-state structure. A solution IR spectrum (in hexane) of **2** is included in Figure 3a, which shows *four* CO bands at 1997 (vs), 2063 (m), 2069 (vs), and 2113 (m) cm^{-1}. The positions of the two higher intensity bands are close to those observed for the CO groups in the parent complex. Hence, these two bands are assigned to the COs attached to the unoxidized Ir center, while the two lower intensity bands are assigned to the COs attached to the oxidized Ir center. A similar pattern has been observed for the CO bands in the complex resulting from a one-center 2-electron oxidative addition of MeI to Ir₂(μ-PPh₂)(μ-PNNP)(CO)₂.[11g]

The ^{1}H NMR spectrum of **2** is fairly simple and is consistent with its solid-state structure. The resonance

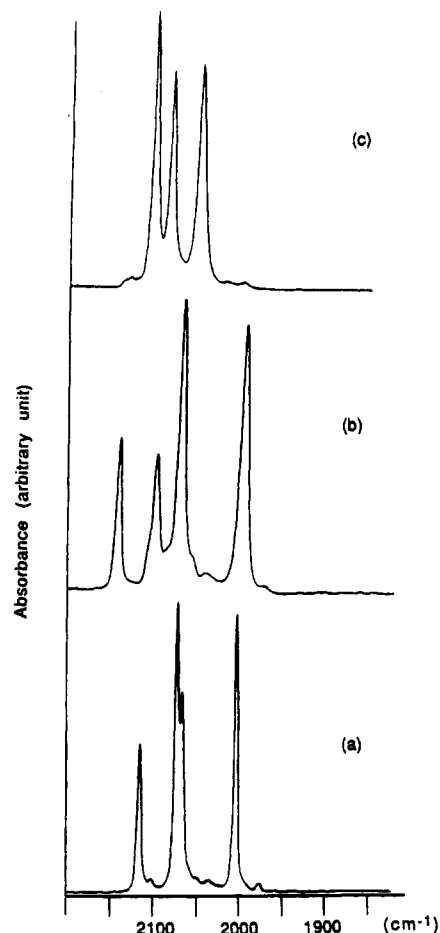**Figure 3.** IR bands in the carbonyl region of (a) Ir₂(Me)(I)[μ-NH(p-tolyl)]₂(CO)₄, (b) Ir₂Cl₂[μ-NH(p-tolyl)]₂(CO)₄, and (c) Ir₂I₂[μ-NH(p-tolyl)]₂(CO)₄. Spectrum a was obtained in hexane, and spectra b and c were obtained in CH₂Cl₂.

for the metal-bound Me group appears at δ 1.99, with half the intensity of the resonance at δ 2.33 due to the two *p*-Me groups. The broad signal at δ 5.08 is assigned to the N–H proton and shows a downfield shift of more than 1.5 ppm relative to the N–H signal in the parent complex. It is clear, based on their equivalency, that the bridging amido groups have retained their *cis* orientation in solution.
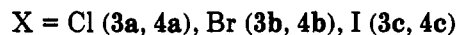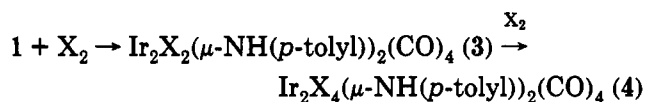
The ^{13}C NMR spectrum of **2** shows, along with the expected resonances for the amido group carbon atoms, two signals at δ 172.8 and 159.5 for the carbonyl groups. By comparing these values with those associated with **1**, we assign the lower field resonance to the CO groups attached to the Ir(I) center and the higher field resonance to the CO groups attached to the Ir(III) center. The resonance due to the Ir-bound Me group appears at δ –4.0. Such a high field value for sp^3 carbon atoms when coordinated to Ir(III) centers is not unprecedented.[13]

Further reaction of **2** with excess MeI produces a reaction mixture which has a broad CO band centered at 2036 cm^{-1}. The product does not appear to be the two methyl iodide addition product, which should give rise to two relatively sharp CO bands, as has been observed for the addition of 2 equiv of HCl or halogens (*vide infra*). We have also considered the possibility that the addition of 2 equiv of MeI promotes reductive elimination of ethane and the generation of Ir₂I₂[(μ-NH(p-tolyl)]₂(CO)₄, where each iridium is in the +2 oxidation state. We have prepared

(13) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: London, 1981; Table 2.8, pp 151–182.

this diiridium complex independently (*vide infra*), and the complex shows three relatively sharp ν(CO) bands. At this point, the identity of the product(s) in question is uncertain and further work is in progress.

Reactions with Halogens. Complex 1 undergoes clean and rapid reactions with halogens in hydrocarbon solvents. The reactions proceed in a stepwise manner, as shown by the following equation.

$$1 + X_2 \xrightarrow{} Ir_2X_2(\mu\text{-NH}(p\text{-tolyl}))_2(CO)_4 \; (3) \xrightarrow{X_2}$$

$$Ir_2X_4(\mu\text{-NH}(p\text{-tolyl}))_2(CO)_4 \; (4)$$

X = Cl (**3a, 4a**), Br (**3b, 4b**), I (**3c, 4c**)

The addition of 1 equiv of Cl_2 gas to a toluene solution of 1 at 0 °C produces a color change from yellow-brown to green in approximately 20 min. After workup, a pale yellow solid can be obtained in ~50% yield. The IR spectrum of the solid in CH_2Cl_2 shows *four* bands at 1992 (s), 2068 (s), 2091 (m), and 2142 (m) cm^{-1}. As shown in Figure 3b, the two lower energy bands are approximately twice as intense as the two higher energy bands. The spectral pattern is very similar to that observed for the MeI oxidative addition product 2; hence we believe that they have similar structures. The two lower energy bands are assigned to the $Ir^I(CO)_2$ fragment, while the two higher energy, and lesser intensity, bands are assigned to the $Ir^{III}(CO)_2$ fragment. Comparison of spectra a and b in Figure 3 reveals that the two higher intensity bands remain virtually unchanged, whereas each of the lower intensity bands for **3a** is shifted to a higher energy by ~30 cm^{-1} compared to those for 2. The shift is consistent with Cl_2 being a better electrophile than MeI, and the relative insensitivity of the Ir(I) center in these two complexes to the changes in the neighboring Ir(III) center suggests very little communication between the two.

The ^{1}H and ^{13}C NMR spectra of **3a** in $CDCl_3$ show it to be a diamagnetic complex, and all of the resonances are observed in the expected regions.

When excess Cl_2 gas is allowed to bubble through a toluene solution of 1, a yellow solution results that shows two ν(CO) bands in the IR at 2148 and 2108 cm^{-1}. The pale yellow solid, **4a**, that can be isolated in good yield from this reaction is formulated as the Ir(III) dimer $Ir_2Cl_4[\mu\text{-NH}(p\text{-tolyl})]_2(CO)_4$. As expected, the positions of the carbonyl bands are not significantly different from those associated with the $Ir^{III}(CO)_2$ fragment of **3a**. The ^{1}H NMR spectrum of **4a** shows a further downfield shift of the –NH– proton relative to that in **3a**, resulting from an increase in the metal's oxidation state. The lower field resonance of the phenyl protons of **4a** are broad, and this, along with the rest of the resonances, shows a downfield shift compared to those of **3a**. We believe that the chloride ligands are terminal, and not bridging, because of the similarities in the ^{1}H NMR and IR spectra of **3a** and the tetraiodo complex **4c** (*vide infra*), whose solid-state structure (being refined) shows four terminal iodo ligands.

The reaction of bromine with 1 proceeds in a manner similar to the reaction with chlorine. The dibromo adduct, **3b**, shows CO bands at 2124 (m), 2074 (m), 2067 (s), and 1991 (s) cm^{-1}. Once again, the medium intensity bands are assigned to the CO ligands attached to the oxidized metal center bearing the bromide ligands. As expected, the CO bands associated with the Ir(I) center have about the same energy as those for 2 or **3a**. Upon the addition

of 2 equiv of Br_2, a yellow product is obtained which is formulated as $Ir_2Br_4[\mu\text{-NH}(p\text{-tolyl})]_2(CO)_4$, **4b**, on the basis of its having two CO bands at 2144 (s) and 2103 (s) cm^{-1}.

Instead of the familiar one-center 2-electron oxidative addition discussed so far, the addition of one equiv of I_2 to 1 produces a two-center 2-electron oxidative addition reaction to give $Ir_2I_2[\mu\text{-NH}(p\text{-tolyl})]_2(CO)_4$, **3c**, having both metal centers in the +2 oxidation state. A diagnostic spectroscopic feature of **3c** that distinguishes it from M(I)–M(III) products is the presence of *three* ν(CO) bands, which in CH_2Cl_2 appear at 2103 (vs), 2082 (s), and 2047 (s) cm^{-1}. As shown in Figure 3c, the lowest energy band of **3c** is shifted by more than 50 cm^{-1} relative to those of 2 and **3a**. The ^{1}H NMR spectrum of **3c** shows two doublets, at δ 7.08 and 7.04, for the phenyl hydrogens, a broad singlet at δ 5.35 for –NH– and a singlet at δ 2.29 for the p-Me group. The ^{13}C NMR spectrum of **3c** is also quite diagnostic. We observe only one resonance, at δ 167.0, for the carbonyl ligands, indicating equivalent Ir centers. The chemical shift is also in between those observed for carbonyl groups coordinated to Ir(I) and Ir(III) centers. On the basis of these evidences, the following structure III is proposed
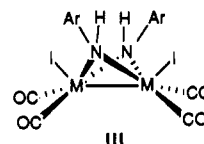
for **3c**. The proposed structure possesses C_{2v} symmetry, which is consistent with its IR and NMR spectra. The product resulting from substitution of one CO group by PPh_3 yields X-ray quality crystals and a structure has recently been determined.[14] The molecule contains one iodide ligand on each metal and a short metal–metal single bond is present.

The tetraiodo complex $Ir_2I_4[\mu\text{-NH}(p\text{-tolyl})]_2(CO)_4$, **4c**, is obtained when 2 equiv of I_2 are added to 1. As expected, of the three Ir(III)–Ir(III) dimers, **4c** features the lowest energy ν(CO) bands, while the tetrachloro complex, **4a**, has the highest energy bands. However, the –NH– proton of the tetraiodo complex shows the highest chemical shift value, δ 6.64, while that of the tetrachloro complex has the lowest chemical shift value, δ 6.10, with an intermediate value for the tetrabromo complex, δ 6.37.

Reaction with HCl. The addition of 1 equiv of HCl forms mainly the Ir(I)–Ir(III) dimer, $Ir_2(H)(Cl)[\mu\text{-NH}(p\text{-tolyl})]_2(CO)_4$, **5**. The synthesis of **5** is always contaminated by the presence of a small amount of the 2 equiv HCl addition product, $Ir_2(H)_2Cl_2(\mu\text{-NH}(p\text{-tolyl}))_2(CO)_4$, **6**, which can be obtained cleanly by passing HCl gas through a solution of 1. An IR spectrum of **6** shows the expected two-band pattern at 2079 and 2126 cm^{-1} for the terminal carbonyl groups. In addition, a broad band at 2183 cm^{-1} can be attributed to the Ir–H stretch. As expected, the ν(CO) bands of **6** have the lowest energy among all of the Ir(III)–Ir(III) dimers reported here. Both **5** and **6** show extensive decomposition in solution as well as in the solid state, which has hindered our attempts to obtain clean ^{13}C NMR spectra of these complexes. However, reasonably clean ^{1}H NMR spectra could be obtained in $CDCl_3$, which are consistent with the formation of a hydride in both cases. For **6**, the only isomer formed contains equivalent

(14) Curley, J. F.; Ahmed, K. J. Results to be published.

Table III. Bond Lengths (Å) and Angles (deg) for 2

	molecule A[a]	molecule B[a]
Ir(1)–Ir(2)	3.209(1)	3.212(1)
Ir(1)–I	2.759(2)	2.771(2)
Ir(1)–C(1)	1.892(17)	1.876(27)
Ir(1)–C(2)	1.897(19)	1.906(15)
Ir(1)–C(3)	2.118(18)	2.128(17)
Ir(2)–C(4)	1.830(22)	1.818(14)
Ir(2)–C(5)	1.830(16)	1.863(23)
Ir(1)–N(1)	2.116(13)	2.122(10)
Ir(1)–N(2)	2.105(10)	2.126(15)
Ir(2)–N(1)	2.112(10)	2.107(15)
Ir(2)–N(2)	2.098(13)	2.108(10)
I–Ir(1)–C(1)	90.5(6)	90.8(6)
I–Ir(1)–C(2)	89.6(6)	92.6(5)
I–Ir(1)–C(3)	177.2(4)	177.8(5)
I–Ir(1)–N(1)	88.9(4)	87.5(3)
I–Ir(1)–N(2)	87.3(3)	87.5(3)
C(1)–Ir(1)–C(2)	91.8(8)	92.7(9)
C(1)–Ir(1)–C(3)	92.1(8)	90.6(8)
C(1)–Ir(1)–N(1)	95.1(7)	95.8(6)
C(1)–Ir(1)–N(2)	171.3(7)	172.6(6)
C(2)–Ir(1)–C(3)	91.5(8)	88.9(6)
C(2)–Ir(1)–N(1)	173.0(6)	171.5(8)
C(2)–Ir(1)–N(2)	96.6(6)	94.6(8)
C(3)–Ir(1)–N(1)	89.7(6)	90.8(5)
C(3)–Ir(1)–N(2)	90.0(5)	90.8(7)
N(1)–Ir(1)–N(2)	76.4(5)	76.9(5)
C(4)–Ir(2)–C(5)	88.6(8)	89.4(8)
C(4)–Ir(2)–N(1)	96.8(6)	96.2(8)
C(4)–Ir(2)–N(2)	173.0(6)	173.8(8)
N(1)–Ir(2)–N(2)	76.7(5)	77.6(5)
Ir(1)–N(1)–Ir(2)	98.7(5)	98.8(5)
Ir(1)–N(2)–Ir(2)	99.5(6)	98.7(5)

[a] The two independent molecules have been arbitrarily labeled as molecule A and molecule B.

hydrido and *p*-tolyl groups, implying that the second equivalent of HCl adds in such a way that the two hydride and the two chloride ligands are on the opposite sides of the dimer. The following is a schematic representation of the proposed structure of **6**.


IV
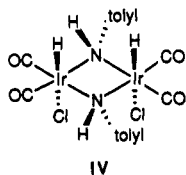
Solid-State Structure of Ir₂(Me)(I)[μ-NH(p-tolyl)]₂-(CO)₄·0.25C₆H₁₄, 2. A pale yellow block-shaped crystal was selected for X-ray structural analysis. The compound was found to crystallize in the centrosymmetric triclinic space group *P*1̄, with two chemically similar but crystallographically independent molecules per asymmetric unit. An ORTEP drawing of one of the molecules is shown in Figure 2, and selected bond lengths and angles are given in Table III. The metal—ligand distances around both metal centers are normal. Although the metal—carbonyl distances for the oxidized Ir(1) appear longer than those for the unoxidized Ir(2), the differences are within 3σ. A consideration of the ionic radii of Ir(I) and Ir(III) would predict an opposite effect; similar observations in the past in cases involving Rh have been explained in terms of different metal—ligand back-bonding between Rh(I) and Rh(III).[11g,15] The geometry around Ir(2) is close to being square-planar, the largest deviation from the ideal value

(15) Meier, E. B.; Burch, R. R.; Muetterties, E. L.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 2661.

being observed in the N(1)—Ir(2)—N(2) angle, 76.7(5)°. Except for a similar deviation in the N(1)—Ir(1)—N(2) angle, the geometry around Ir(1) approaches close to being octahedral. The deviations are most likely due to the particular "bite" angle of the bridging amido groups. The bridging nitrogen atoms are essentially equidistant from both metal centers, and the distances are similar to those observed for the starting complex **1**. However, oxidative addition produces significant changes in the Ir₂(μ-N=)₂ fragment: the two iridium centers move farther apart and the Ir₂N₂ "butterfly" core flattens compared to the case in the starting complex. The "hinge" angle, defined by the angle at which the planes Ir(1)—Ir(2)—N(1) and Ir(1)—Ir(2)—N(2) intersect, is 145.6° in the oxidized complex compared to 118.5° in the starting complex. Quite expectedly, the Ir—Ir distance in **2** is ~0.3 Å longer than that in the starting complex; however, this distance is much shorter than that observed in the Rh(I)—Rh(III) dimer [Rh₂(μ-PPh₂)(CO)₂(PNNP)MeI] (3.766 Å)[11g] and falls in the range of values claimed to imply metal—metal contact for square-planar Rh and Ir complexes. The greater intermetallic separation has stretched out the Ir(1)—(μ-N)—Ir(2) bond angles, from an average value of 88.8° in the starting complex to an average value of 99.1° in the MeI adduct. Due to the combination of a greater separation of the two Ir centers and a flattening of the butterfly core, the Ir(1)—N(1)—N(2) and Ir(2)—N(1)—N(2) planes intersect at a more obtuse angle in **2** (153.1°) than in the starting complex (124.6°). The pyramidality around the bridging nitrogen atoms in **2** is slightly larger (average value of the sum of three angles is 338°) than that in the starting complex (average value is 332°).

Bond lengths and angles in the two *p*-tolyl rings are normal. Possibly due to packing interactions, a slight skewing of the two rings with respect to each other is observed.

Discussion

Among the many studies of oxidative addition reactions to dinuclear metal complexes containing one or more bridging groups, the work of Stobart et al.[8] and Bosnich et al.[11h,i] on dirhodium and diiridium complexes are of particular relevance to the present study. In a series of papers, Stobart et al. have examined the oxidative addition reactions of alkyl halides and halogens with [Ir(μ-pz)L₂]₂, **V**, where pz = pyrazolyl and L₂ = COD, CO, or a mixture

V
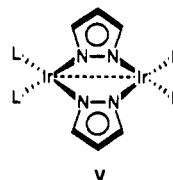
of CO and PPh₃. These complexes feature a short metal-metal contact, ~3.0 Å. The addition of 1 equiv of halogens or MeI produces a two-center 2-electron oxidation with the formation of a metal—metal bond. However, oxidative addition of MeI or MeC(O)Cl to the following PNNP bridged complex, **VI**, initially gives a one-center 2-electron addition product which, in a subsequent step, yields the final M(III)–M(III) product. Due to the particular geometric constraints of the bridging PNNP ligand, the two metal centers in the starting complex are held at a distance that falls outside the range for a formal metal—metal

VI
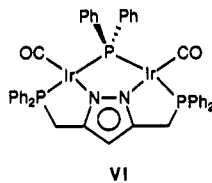
contact. One can argue that the large separation causes oxidative addition to occur first to only one metal and, since the second oxidative addition is much slower, that a cooperativity effect through the bridging groups deactivates the second metal toward further oxidative addition.

In light of the above results, our results pose a new set of anomalies. Except for the addition of I_2, all of the oxidative addition reactions that we have studied proceed in two steps, first giving a M(I)–M(III) complex and then a M(III)–M(III) complex. This behavior cannot be attributed to any large metal–metal separation. Furthermore, the observed mode of addition of I_2 proves that the diiridium framework in the starting complex 1 is able to afford an Ir(II)–Ir(II) framework with a metal–metal single bond. The possibility, therefore, exists that the formation of the M(I)–M(III) dimer is kinetically controlled and the M(II)–M(II) form is the thermodynamic product, or vice

versa. However, we have not yet found any evidence that the addition of I_2 goes through a M(I)–M(III) intermediate or that the other M(I)–M(III) dimers convert to the M(II)–M(II) form, at least at ambient temperatures. Further mechanistic studies are in progress to explore these possibilities. It should be noted here that the addition of halogens to $[Ir(\mu\text{-SR})L_2]_2$ (L = CO, phosphines, and phosphites) initially produces a two-center 2-electron oxidative addition product which ultimately yields the final Ir(III)–Ir(III) dimer.[11c] Studies to elucidate the mechanism of the oxidative addition reactions reported here and further reactivity of the oxidative addition products are underway.