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Anionic μ-Imido Complexes of Iridium(I): Synthesis and Spectroscopic Characterization

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The bridging amido ligands in $\mathrm{Ir_2[\mu\text{-}NH(\mathit{p}\text{-}tolyl)]_2(CO)_4}$, **1**, undergo deprotonation by ^{t}BuLi in a stepwise manner. The first deprotonation product is a monoanionic μ-amido/μ-imido complex of formula $\mathrm{LiIr_2[\mu\text{-}NH(\mathit{p}\text{-}tolyl)][\mu\text{-}N(\mathit{p}\text{-}tolyl)](CO)_4{\cdot}2THF}$, **2**, which shows three CO bands in the IR, similar to the pattern observed for **1**. However, the bands are shifted to lower energy by an average of $\sim$50 cm^{-1}. The second deprotonation step produces a dianionic bis(μ-imido) complex, $\mathrm{Li_2Ir_2[\mu\text{-}N(\mathit{p}\text{-}tolyl)]_2(CO)_4{\cdot}3THF}$, **3**, in which the CO bands are shifted by another 25 cm^{-1}(average). The high solubility of the ionic complexes in hydrocarbon solvents, coupled with the number of THF molecules available for each lithium ion, suggests strong cation−anion interaction, most likely at the imido nitrogens. Variable-temperature NMR studies have detected the formation of aggregates in solution for **2**. Complex **3** possesses two inequivalent lithium ions that produce separate ^{7}Li signals at temperatures below 0 °C but produce an average signal around room temperature. The THF molecules in **2** and **3** can be displaced by 12-Crown-4 to give complexes **2·Crown** and **3·Crown**, in which the lithium ions are encapsulated by the crown ether. The reaction of **3** with $\mathrm{(PPh_3)AuCl}$ generates a tetranuclear complex, $\mathrm{[(CO)_2Ir(\mu\text{-}N(\mathit{p}\text{-}tolyl))Au(PPh_3)]_2}$, **4**.

Introduction

The imido group is a ubiquitous ligand in transition metal chemistry.[1] Due to their high π-electron-donating capability, these ligands have been used to stabilize the high oxidation states of early transition metals. Since *late* transition metals are usually unable to form strong ligand-to-metal π bonds, imido complexes involving these metals are expected to show high ligand-based nucleophilicity. Such characteristics can lead to synthetically useful reactions of coordinated imido ligands, such as insertion of alkenes or carbon monoxide into the metal−imido bond. However, relatively very few studies have been reported for imido complexes involving late transition metals.[2−4] As part of our interest in studying highly basic imido complexes of low-valent group 9 metals, we report here the synthesis and characterization of novel *mono-* and *dianionic* imido complexes containing iridium in the +1 oxidation state. The anionic complexes are obtained by deprotonation of the bridging amido ligands in $\mathrm{Ir_2[\mu\text{-}NH(\mathit{p}\text{-}tolyl)]_2(CO)_4}$, **1**, which we reported earlier.[5]

Experimental Section

All preparations were carried out under N_2 in an inert atmosphere drybox (Vacuum Atmospheres). Solvents were distilled twice and were stored in the drybox. Hexanes were distilled from P_2O_5 and CaH_2, and toluene and THF were distilled from Na/K alloy and benzophenone. $\mathrm{Ir_2[\mu\text{-}NH(C_6H_4Me)]_2(CO)_4}$ was prepared as described previously.[5a] $\mathrm{(PPh_3)AuCl}$ was purchased from Strem Chemical Co. and was recrystallized once from benzene prior to use. ^{t}BuLi (1.6 M in pentane) was purchased from Aldrich Chemical Co. Deuterated solvents were purchased from Cambridge Isotope Laboratories and were dried over 4-Å molecular sieves.

Infrared spectra were recorded on a Nicolet 6000 series FT-IR instrument. ^{1}H, ^{13}C, ^{31}P, and ^{7}Li NMR spectra were obtained on a Bruker 500 MHz instrument. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Syntheses. $\mathbf{LiIr_2[\mu\text{-}NH(C_6H_4Me)][\mu\text{-}N(C_6H_4Me)](CO)_4{\cdot}2THF}$, 2. The bis(amido) complex $\mathrm{Ir_2[\mu\text{-}NH(C_6H_4Me)]_2(CO)_4}$, **1** (0.10 g, 0.14 mmol), was dissolved in THF (20 mL) in a N_2-filled drybox, and 1 equiv of ^{t}BuLi (0.16 M in hexane) was added dropwise at room temperature. Immediate darkening of the solution indicated the onset of a reaction. Once the addition was complete, the solution was stirred for 5 min, after which it was reduced in volume to ca. one-third and hexane was added to precipitate **2** as a red solid. Recrystallization of the red solid from toluene/hexane afforded analytically pure sample. Yield: $\sim$76%. Anal. Calcd for $\mathrm{LiIr_2[\mu\text{-}NH(C_6H_4Me)][\mu\text{-}N(C_6H_4Me)](CO)_4{\cdot}2THF}$: C, 36.33; H, 3.64; N, 3.26. Found: C, 36.23; H, 4.14; N, 2.94. IR (carbonyl region), THF, cm^{-1}: 2015 (w), 1992 (s), 1930 (s). ^{1}H NMR (500 MHz, C_6D_6): δ 7.65, 7.10, 6.91 (m, 8H, C_6H_4Me), 2.08, 2.29 (s, 6H, C_6H_4Me), 2.89 (s, 1H, N*H*), 3.61, 1.55 (m, 16H, THF). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 177.5, 185.5 (Ir−*C*O). ^{7}Li NMR (toluene-d_8, 30 °C (4.0 M $LiClO_4$ in D_2O as external reference)): δ −3.1.

$\mathbf{Li_2Ir_2[\mu\text{-}N(C_6H_4Me)]_2(CO)_4{\cdot}3THF}$, 3. A procedure analogous to the one described above, except for adding 2 equiv of ^{t}BuLi instead of 1 equiv, was used. Recrystallized yield: $\sim$79%. Anal. Calcd for $\mathrm{Li_2Ir_2[\mu\text{-}N(C_6H_4Me)]_2(CO)_4{\cdot}3THF}$: C, 38.46; H, 2.99; N, 2.99. Found: C, 36.01; H, 3.82; N, 2.89. The observed values correspond to a formula with *two* THF molecules (Calcd: C, 36.11; H, 3.50; N, 3.24). IR (carbonyl region), THF, cm^{-1}: 1992 (m), 1968 (s), 1905 (s). ^{1}H NMR (500 MHz, C_6D_6): δ 7.60, 7.05 (d, 8H, C_6H_4Me), 2.31 (s, 6H, C_6H_4Me), 3.50, 1.03 (m, 16H, THF). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 183.1 (Ir−CO). ^{7}Li NMR (toluene-d_8, 30 °C): δ 1.8.

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(2) Terminal imido complexes: (a) Glueck, D. S.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2719. (b) Glueck, D. S.; Wu, J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 2041. (c) Ashley-Smith, J.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1972**, 1805. (d) Ashley-Smith, J.; Green, M.; Mayne, N.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1969**, 409.

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$LiIr_2[\mu\text{-}NH(C_6H_4Me)][\mu\text{-}N(C_6H_4Me)](CO)_4(12\text{-}Crown\text{-}4)$, 2·Crown. Complex **2** (0.10 g, 0.12 mmol) was dissolved in toluene (15 mL), and 12-Crown-4 (19 μL, 1 equiv) was added. The reaction mixture was stirred for 10 min, over which period a red precipitate appeared. The precipitate was filtered off, washed with hexane, and pumped to dryness. The filtrate was concentrated in volume and cooled to −10 °C for 2 days to produce more red precipitate. Combined yield: 72%. IR, THF, cm^{-1}: 2017 (w), 1990 (s), 1933 (s). ^1H NMR (toluene-d_8, 27 °C): δ 2.31 (s, C_6H_4Me, overlapping with toluene-d_8 Me resonance), 3.09 (br s, −N*H*−), 3.63 (s, $-CH_2CH_2-$), 7.09 and 7.26 (d, $-C_6H_4Me$).

$Li_2Ir_2[\mu\text{-}N(C_6H_4Me)]_2(CO)_4\cdot 2(12\text{-}Crown\text{-}4)$, 3·Crown. A procedure similar to the synthesis of **2·Crown** was employed, except that 2 equiv of 12-Crown-4 was used. Yield: 50%. Anal. Calcd for $Li_2Ir_2[\mu\text{-}N(C_6H_4Me)]_2(CO)_4(12\text{-}Crown\text{-}4)\cdot 0.5C_6H_5Me$: C, 42.2; H, 4.7; N, 2.4. Found: C, 41.7; H, 5.1; N, 2.4. IR, THF, cm^{-1}: 1990 (w), 1970 (s), 1903 (s). ^1H NMR (C_6D_6): δ 7.30−6.99 (m, 8H, C_6H_4Me), 3.43 (br s, 32H, $-CH_2CH_2-$), 2.10 (s, 6H, C_6H_4Me). ^7Li NMR (toluene-d_8): δ −3.8.

$[(CO)_2Ir(\mu\text{-}N(C_6H_4Me))Au(PPh_3)]_2$, 4. To a solution of $(PPh_3)AuCl$ (0.05 g, 0.1 mmol) in THF (10 mL) was added **3** (0.05 g, 0.05 mmol), also in THF (10 mL). The original red-brown color of **3** changed to green-brown. The reaction mixture was allowed to stir for 15 min, after which the solution was stripped to dryness. The solid residue was extracted with toluene (25 mL), and the exract was filtered through a 0.5 in. pad of Celite. The volume of the clear filtrate was reduced to about half, and hexane was added. Cooling the mixture to −10 °C for 24 h yielded green-brown microcrystalline solids, which were collected by filtration, washed with hexane, and dried under vacuum. Yield: 58%. Anal. Calcd for $Ir_2[\mu\text{-}N(C_6H_4Me)]_2(CO)_4[Au(PPh_3)]_2$: C, 39.91; H, 2.73; N, 1.72. Found: C, 39.38; H, 2.93; N, 1.61. ^1H NMR (500 MHz, C_6D_6): δ 7.89, 6.79 (d, 8H, C_6H_4Me), 7.65, 6.95 (m, 30H, $P(C_6H_5)_3$), 2.15 (s, 6H, C_6H_4Me). ^{31}P NMR (202.5 MHz, C_6D_6): δ 27.3.

Reactions of 2 and 3 with Water. Complex **3** was dissolved in wet THF (containing ~0.1% H_2O v/v), and the solution was examined by IR spectroscopy. A rapid and clean conversion of **3** to **2** and eventually to **1** was observed by monitoring the CO bands. The identity of the final product was further confirmed by ^1H NMR spectroscopy.

Results and Discussion

Synthesis. The imido complexes were prepared by addition of ^tBuLi to **1**, causing removal of the amido hydrogens in a stepwise manner:

$$\begin{tikzcd}
\mathrm{Ir_2[\mu\text{-}NH(\mathit{p}\text{-}tolyl)]_2(CO)_4}\ (\mathbf{1}) \arrow[d, "{^t\mathrm{BuLi}\ \mathrm{THF}}"', "{-\,^t\mathrm{BuH}}"] \\
\mathrm{LiIr_2[\mu\text{-}NH(\mathit{p}\text{-}tolyl)][\mu\text{-}N(\mathit{p}\text{-}tolyl)](CO)_4\cdot(THF)_2}\ (\mathbf{2}) \arrow[d, "{^t\mathrm{BuLi}\ \mathrm{THF}}"', "{-\,^t\mathrm{BuH}}"] \\
\mathrm{Li_2Ir_2[\mu\text{-}N(\mathit{p}\text{-}tolyl)]_2(CO)_4\cdot(THF)_3}\ (\mathbf{3})
\end{tikzcd}$$

As shown in Figure 1, the pattern of CO bands for both **2** and **3** is very similar to that observed for **1**, but these bands are now shifted to lower energies by an average of 58 and 84 cm^{-1}, respectively. These large shifts are indicative of interaction between the nitrogen-based $p\pi$ orbital and the filled $d\pi$ orbitals (d_{xz} and d_{yz}, if the Ir−N bonds are taken as the x and y axes) on each Ir, thus enhancing back-bonding to CO.

On the basis of the observed similarities in the carbonyl band patterns of **1**−**3**, we conclude that the basic structures of the diiridium core in the three complexes are similar. As we reported earlier,[5] the solid-state structure of **1** reveals a bent $Ir_2[\mu\text{-}NH(p\text{-}tolyl)]_2$ core with a short Ir−Ir nonbonded distance of 2.933(1) Å. We have argued that the metal−metal interaction is maintained in solution and is responsible for the appearance of three CO bands in the solution IR spectrum. We envision a similar bent structure for both **2** and **3**. From a structural point of view, a critical issue to consider here is the coordination environment around the Li^+ ions and the extent of their interaction with the anions. The evidences supporting Li−anion interaction are (i) the solubility of both **2** and **3** in nonpolar solvents, such as toluene and benzene, (ii) the number of THF molecules present in the complexes, and (iii) ^7Li NMR spectroscopy. We believe that the lithium ions are coordinated to the nitrogen atom of the bridging imido ligands, since these sites bear the highest electron density as evidenced during protonation reactions (*vide infra*). Any interaction of the lithium ions with the CO ligands can also be ruled out on the basis of the sharpness of the CO bands in the IR spectrum.

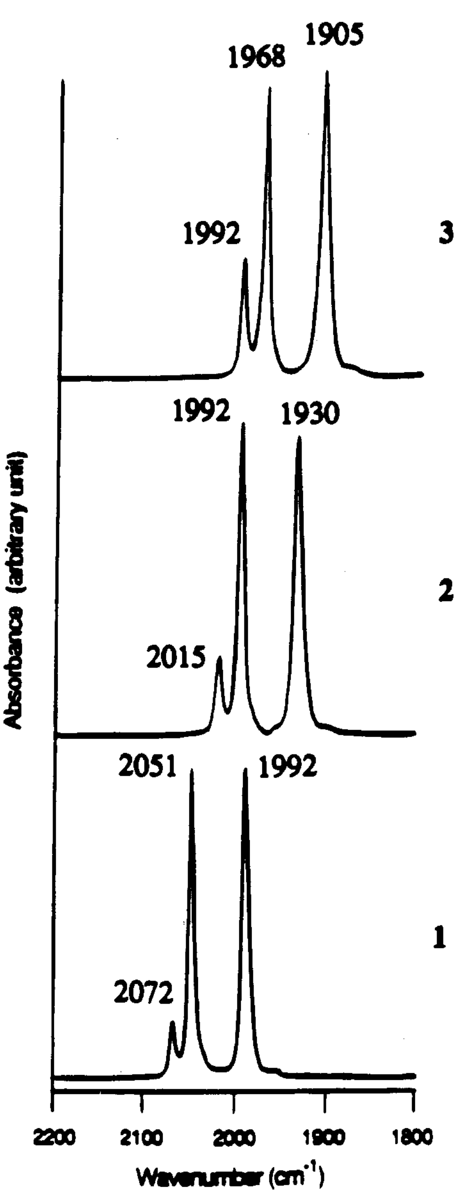

Figure 1. IR bands for the carbonyl ligands in **1**−**3**.

Structural Characterization of 2 by Variable-Temperature NMR Spectroscopy. Both elemental analysis and integration of signal intensities in the ^1H NMR spectrum (C_6D_6) of **2** indicate the presence of two THF molecules per Li^+ ion. The most commonly observed coordination numbers of complexed lithium ions are 4 and 3.[6] Therefore, the lithium ion in **2** is

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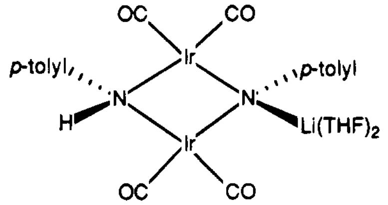
[6] (a) Bauer, W.; Schleyer P. v. R. in *Advances in Carbanion Chemistry*; Snicchus, V., Ed.; JAI Press Inc.: Greenwich, CT, 1992; Vol. 1, p 89. (b) Li, J. J.; Sharp, P. R. *Inorg. Chem.* **1994**, *33*, 183.

most probably coordinated by the imido nitrogen and two THF molecules. Such an arrangement will render the two *p*-tolyl groups inequivalent, as is observed in the room-temperature ^{1}H NMR spectrum shown in Figure 2a. The spectral features are consistent with the structure



The ^{7}Li NMR spectrum at 30 °C (in toluene-d_8) shows a single line at δ −3.1 with a small shoulder centered at δ −2.0. Upon cooling of the sample, the spectrum changes dramatically, as can be seen in Figure 2b. At −3 °C, two distinct resonances are observed. This pattern changes on further cooling, and at −48 °C, two sharp signals and one broad signal result. The sharp signal at δ −3.7 begins to decrease in intensity again as the sample is cooled further, and at the lowest temperature limit allowable by the solvent (−83 °C), two signals are observed. The ^{1}H NMR spectrum, on the other hand, does not undergo any significant change initially upon cooling; however, when the sample is cooled to −45 °C, two of the aromatic doublets begin to broaden and eventually disappear in the baseline at −73 °C. This spectral behavior of **2** clearly suggests a varying degree of aggregation in solution, and the concentrations of the aggregates vary as the temperature is changed. Such behavior is well-known for alkyllithium compounds.[7] The surprising observation that the number of resonances in the ^{1}H NMR spectrum remains unchanged as temperature is lowered probably indicates that aggregation does not greatly affect the local symmetry of the *p*-tolyl groups. The broadening of a pair of aromatic doublets at very low temperatures indicates hindered rotation of one of the *p*-tolyl groups, most probably the one adjacent to the lithium ion.

We plan to carry out a detailed spectroscopic analysis of **2** labeled with ^{15}N and ^{6}Li, which will shed light on the nature of the aggregates through ^{15}N−^{6}Li coupling interactions. Results of this study will be published.

When 12-Crown-4 (1,4,7,10-tetraoxacyclododecane) is reacted with **2**, a new complex is formed, labeled **2·Crown**, in which the lithium ion is believed to be encapsulated by the crown ether (no THF was found). The ^{1}H NMR spectrum of this complex shows *one* Me resonance and *two* aromatic doublets, indicating that when the lithium ion is no longer coordinated to the imido nitrogen, the two *p*-tolyl groups become equivalent through either rapid hopping of the amido hydrogen between the two bridging nitrogens or formation of an −N−H−N− bridge.

Structural Characterization of 3 by Variable-Temperature NMR Spectroscopy. The formulation of complex **3** as having three coordinated THF molecules is based on relative integrated intensities of the various signals in the ^{1}H NMR spectrum. However, elemental analysis results indicate the presence of two THF molecules. Such anomaly, we suspect, is due to decomposition of the complex during sample handling in the laboratory that performed the analysis or to the fact that one of

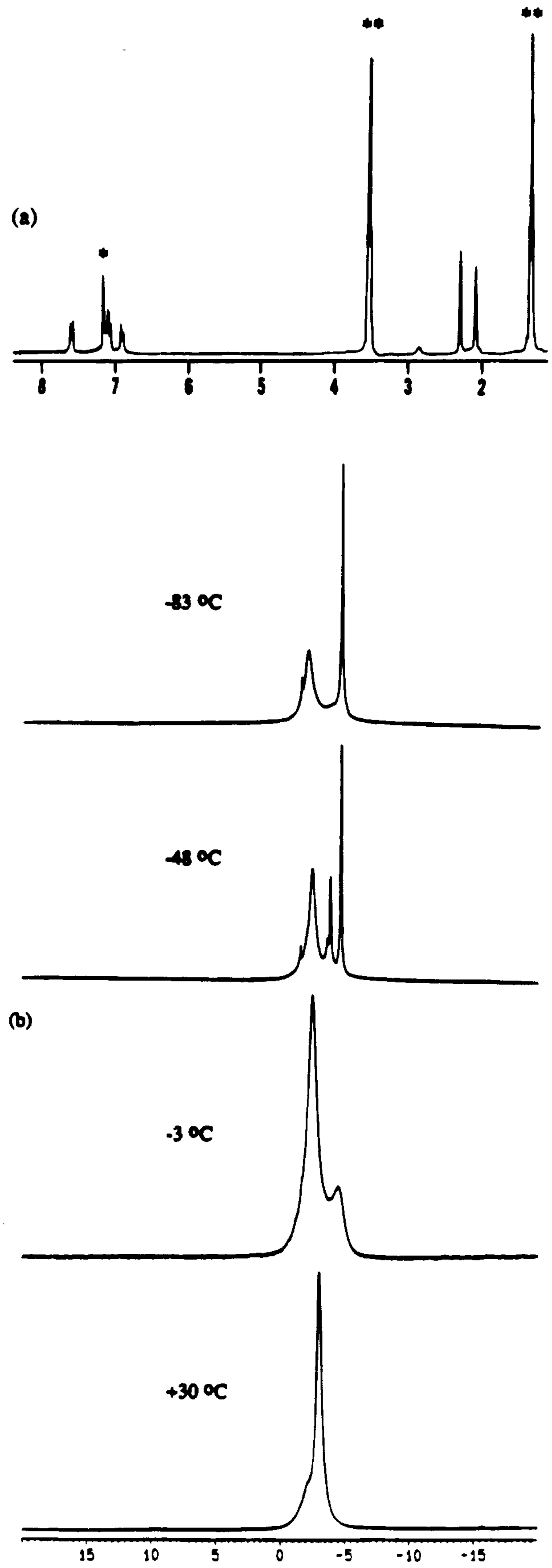


Figure 2. (a) ^{1}H NMR spectrum of **2** in C_6D_6. An asterisk denotes the protio residue of C_6D_6, and two asterisks denote signals for the THF molecules. (b) ^{7}Li NMR spectra (toluene-d_8) of **2** at different temperatures.

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[7] Thomas, R. D.; Clarke, M. T.; Jensen, R. M.; Young, T. C. *Organometallics* **1986**, *5*, 1851 and references therein.

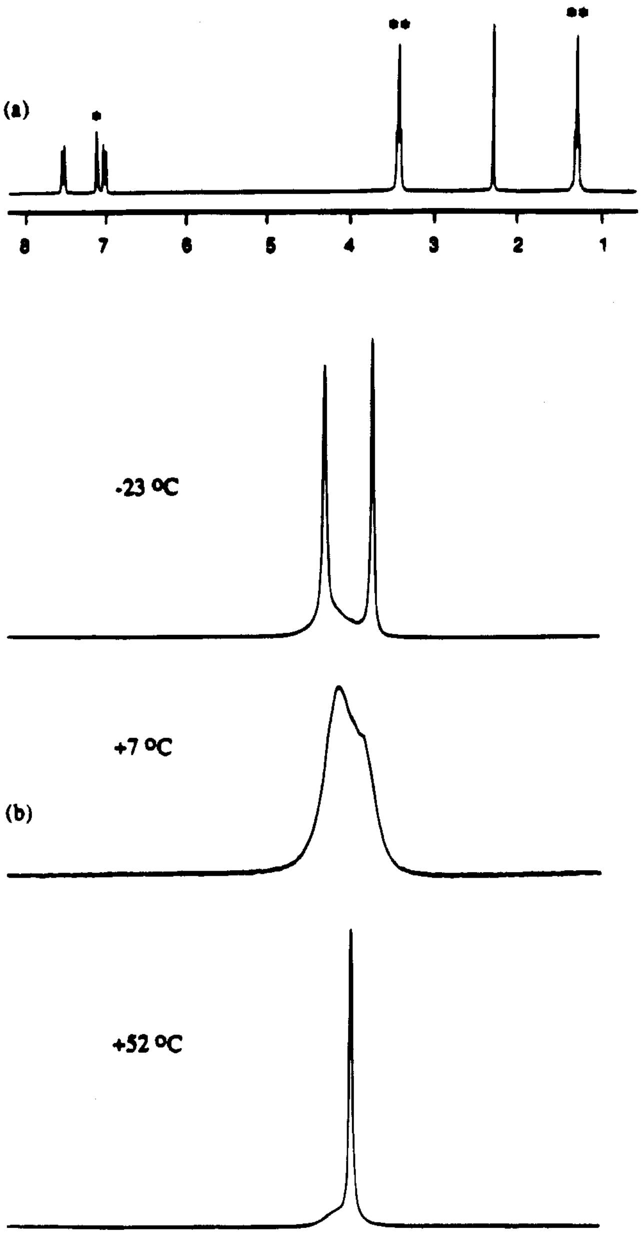
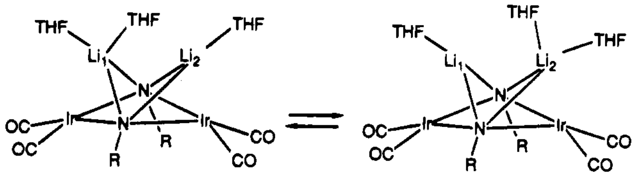


Figure 3. (a) ^{1}H NMR spectrum of **3** in C_6D_6. An asterisk denotes the protio residue of C_6D_6, and two asterisks denote signals for the THF molecules. (b) ^{7}Li NMR spectra (toluene-d_8) of **3** at different temperatures.

the THF molecules dissociates in the solid state during shipment and storage of the sample.

The room-temperature ^{1}H NMR spectrum of **3** in benzene-d_6 (Figure 3) shows one Me resonance (δ 2.25) and two doublets (δ 7.00 and 7.55) for the aromatic hydrogen atoms, indicating equivalent *p*-tolyl groups in the anion of **3**. The ^{7}Li NMR spectrum at +52 °C shows a single line at δ +1.8, with a small shoulder centered at δ +3.2. As the temperature is lowered, the spectrum begins to change, ultimately giving two singlets at −23 °C. At lower temperatures, the two signals remain virtually unaltered. Throughout this temperature range, no change was observed in the ^{1}H NMR spectrum. To account for the presence of three coordinated THF molecules and to rationalize the variable-temperature NMR behavior, we propose a structure in which the two lithium ions have different coordination number—one coordinated by two THF molecules and two imido nitrogens and the other coordinated by one THF molecule and two imido nitrogens. At higher temperatures, rapid exchange of THF molecules can present an average environment for both lithium ions, thus producing a single ^{7}Li resonance; slower exchange at lower temperatures will give different ^{7}Li resonances. The proposed structure



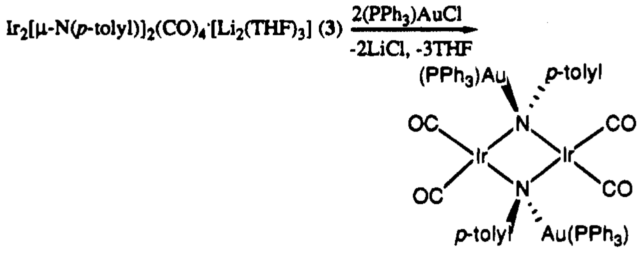
maintains C_s symmetry during slow exchange of the THF molecules.

Of course, aggregation is also a very strong possibility for **3** and may account for the two signals in the ^{7}Li NMR spectrum. As with **2**, we plan a thorough investigation of the solution behavior of **3** by using ^{6}Li- and ^{15}N-labeled complexes.

Addition of 12-Crown-4 to **3** causes rapid displacement of all the coordinated THF molecules and affords $Ir_2[\mu\text{-}N(p\text{-tolyl})]_2(CO)_4 \cdot 2Li(12\text{-Crown-4})$, **3·Crown**, as a red crystalline product. The ^{1}H NMR spectrum of the anion in **3·Crown** is identical to that in **3**.

In spite of repeated attempts, we have so far failed to obtain crystals of **2** and **3**, or their crown ether complexes, that are suitable for X-ray crystallography. Both **2** and **3** crystallize from THF/hexane solvent mixture as long needles; however, removal of the crystals from the mother liquor causes rapid (in less than a minute) loss of their crystallinity, which has thwarted our efforts of obtaining an X-ray crystal structure. Attempts are, however, continuing.

Reactivity. Both **2** and **3** react *extremely* rapidly with water, which converts **3** to **2**, and **2** to **1**. As expected, the conversion of **3** to **2** occurs faster than that of **2** to **1**. The regeneration of **1** from **3** and **2** in a clean and quantitative fashion confirms the structural assignment of the anionic complexes. Other electrophiles are also found to react with the imido groups in these complexes. For example, $(PPh_3)AuCl$ forms a tetranuclear complex, $[(CO)_2Ir(\mu\text{-}N(p\text{-tolyl}))Au(PPh_3)]_2$, **4**, when reacted with **3**. Although at least two isomers of **4** having the *p*-tolyl (or $AuPPh_3$) groups either mutually cis or trans are possible, we observe only one set of resonances at room temperature in the ^{1}H NMR spectrum. The $^{31}P\{^1H\}$ NMR spectrum also displays one single resonance. At temperatures of −35 °C and lower, however, two ^{31}P resonances are observed, indicating the presence of two isomers.



$$Ir_2[\mu\text{-}N(p\text{-tolyl})]_2(CO)_4 \cdot [Li_2(THF)_3]\ (3) \xrightarrow[-2LiCl,\ -3THF]{2(PPh_3)AuCl}$$

4

Conclusion. This paper describes the synthesis of the first examples of anionic μ-amido/μ-imido, **2**, and bis(μ-imido), **3**, complexes. In the absence of a crystal structure, the structural characterization of these complexes is based on spectroscopic evidence. The similarity of the CO band patterns of the anionic complexes to that of **1** is taken as an indication that the anions are dimeric in nature. ^{1}H and ^{7}Li NMR spectral analyses of the anioic complexes reveal the presence of aggregates in solution. The imido centers in **2** and **3** are extremely basic, as evidenced by their rapid reactions with H_2O. The imido groups have begun to show high reactivity toward a variety of electrophiles, including transition metal fragments, thus making it possible to access heterobimetallic complexes with great ease. We are currently exploring the reactivity of **2** and **3** toward small molecules, such as CO, CO_2, alkenes, and alkynes.

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