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Communications

Mononuclear Arylamido Complexes of Iridium(I)

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Summary: The preparation and the first structural characterization of arylamido complexes of Ir(I), having the general formula trans-Ir(CO)(NHAr)(PPh$_3$)$_2$, where Ar = Ph (1), p-C$_6$H$_4$Me (2), 2,6-C$_6$H$_3$Me$_2$ (3), are described. Preliminary results of their facile insertion reactions with CO and CO$_2$ are also discussed.

Although the chemistry of amido (NHR$^-$ or NR$_2^-$) complexes has been extensively studied for high-oxidation-state early transition metals,[1] similar studies involving late transition metals are relatively few. There has been a recent surge in interest in the chemistry of such complexes[2-5] containing the metals Ru(II), Ir(III), Pd(II), and Pt(II). Surprisingly, there has been no systematic study reported for Rh(I) and Ir(I). As part of an initiative to synthesize and characterize alkylamido and arylamido complexes of low-valent Rh and Ir,[6] we report here the preparation and characterization of the complexes *trans*-Ir(CO)(NHAr)(PPh$_3$)$_2$, where Ar = C$_6$H$_5$ (1), *p*-C$_6$H$_4$Me (2), 2,6-C$_6$H$_3$Me$_2$ (3), including the X-ray structure of 2. Complexes 1–3 are the only mononuclear Ir(I) species containing an alkyl- or arylamido ligand prepared to date, other than the reported synthesis of Rh(PPh$_3$)$_2$[N(SiMe$_3$)] by Lappert et al.[7] Moreover, the crystal structure of 2 is the first structural characterization of such a complex. We also provide the preliminary report of a facile CO insertion into the metal–amide bond of these complexes.

The complexes were prepared by the simple metathesis reaction between LiNHAr and Vaska's complex, *trans*-Ir(CO)Cl(PPh$_3$)$_2$. In a typical reaction, between 2.5 and 3 equiv of LiNHAr in THF was added to a THF solution of Vaska's complex in an inert-atmosphere drybox and the mixture was stirred for approximately 10 min. Removal of THF, followed by extraction into toluene and filtration through Celite, yielded a yellow-orange crystalline solid upon reducing the volume of the toluene

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(1) For a comprehensive review of early-transition-metal amido complexes, see: Chisholm, M. H.; Rothwell, I. P. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, England, 1987; Vol. 2, p 161.

(2) (a) Bryndza, H.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163 and references therein. (b) Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1 and references therein.

(3) (a) Glueck, D. S.; Bergman, R. G. *Organometallics* **1991**, *10*, 1479. (b) Glueck, D. S.; Winslow, L. J. N.; Bergman, R. G. *Organometallics* **1991**, *10*, 1462. (c) Koelliker, R.; Milstein, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 707. (d) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738. (e) Ge, Y.-W.; Peng, F.; Sharp, P. R. *J. Am. Chem. Soc.* **1990**, *112*, 2632. (f) Sharp, P. R.; Ge, Y.-W. *J. Am. Chem. Soc.* **1987**, *109*, 3796. (g) Ge, Y.-W.; Sharp, P. R. *J. Am. Chem. Soc.* **1990**, *112*, 3667. (h) Ge, Y.-W.; Sharp, P. R. *Organometallics* **1988**, *7*, 2234.

(4) (a) Park, S.; Roundhill, D. M.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 3972. (b) Villanueva, L. A.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1992**, *11*, 2963. (c) Cowan, R. C.; Trogler, W. C. *Organometallics* **1987**, *6*, 2451. (d) Cowan, R. C.; Trogler, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4750.

(5) (a) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *Organometallics* **1991**, *10*, 1875. (b) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 6499. (c) Martin, G. C.; Palenick, G. J.; Boncella, J. M. *Inorg. Chem.* **1990**, *29*, 2027. (d) Joslin, F. L.; Johnson, M. P.; Mague, J. T.; Roundhill, D. M. *Organometallics* **1991**, *10*, 41. (e) *Organometallics* **1991**, *10*, 2781. (f) Martin, G. C.; Boncella, J. M.; Wucherer, E. J. *Organometallics* **1991**, *10*, 2804.

(6) Kolel-Veetil, M. K.; Rahim, M.; Edwards, A. J.; Rheingold, A. L.; Ahmed, K. J. *Inorg. Chem.* **1992**, *31*, 3877.

(7) Cetinkaya, B.; Lappert, M. F.; Torroni, S. *J. Chem. Soc., Chem. Commun.* **1979**, 843.

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solution. All three complexes were characterized by elemental analysis, IR spectroscopy, NMR spectroscopy,[8] and in the case of 2, single-crystal X-ray diffraction studies.[9]

The formation and purity of the amido complexes can be conveniently monitored by observing their carbonyl stretching bands in the infrared. All three complexes show very similar carbonyl stretching frequencies,[8] being nearly 20 cm^{-1} lower than that for Vaska's complex. This is in agreement with Caulton et al., who have argued in a number of recent publications[10-12] that the lower ν(CO) values that occur when an alkoxide ligand is coordinated are indicative of the presence of some degree of ligand-to-metal π donation, even for late transition metals. As judged from the ν(CO) values, the Ir centers in the amido complexes appear to have electron densities that are comparable to those observed for the metal centers in the structurally analogous aryloxy analogs of Vaska's complex.[13]

The solution NMR spectra of 1–3 are consistent with a square-planar *trans* geometry of the complexes. The resonances for the phenyl hydrogens of the arylamido ligands appear between δ 6.2 and 6.8, and their multiplicity features are consistent with free rotation of the phenyl ring on the NMR time scale. For each complex, the N-*H* hydrogen of the amido ligand displays a reasonably sharp resonance, with very similar chemical shifts for 1 and 2 (*ca.* 2.7 ppm). The N-H resonance for 3, however, is shifted to higher fields by *ca.* 1 ppm. A weaker ligand–metal bond in 3, relative to that in 1 and 2, can cause an upfield shift of the resonance. However, this does not appear to be the case, since IR spectroscopy clearly shows that the ligand–metal bonding in all three complexes is very similar. We are probing the cause of this anomalous behavior. The $^{31}P\{^1H\}$ NMR spectra of all three complexes show one singlet at around 24 ppm, consistent with a *trans* disposition of the phosphine ligands in each complex.

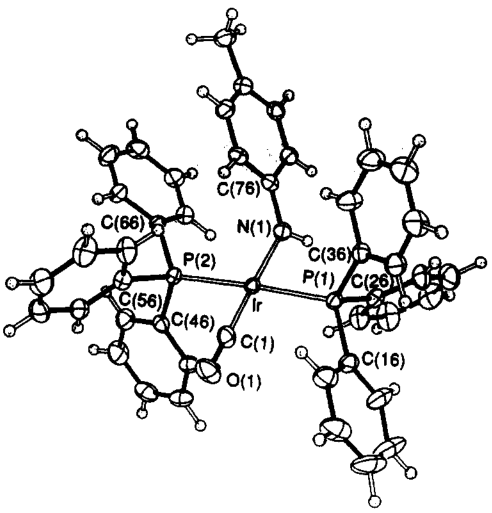

Figure 1. ORTEP diagram of 2. Selected bond lengths (Å) and angles (deg): Ir–P(1) = 2.314(1), Ir–P(2) = 2.334(1), Ir–N(1) = 2.041(3), Ir–C(1) = 1.811(4), C(1)–O(1) = 1.174(6), N(1)–C(76) = 1.385(5); P(1)–Ir–P(2) = 175.3(1), N(1)–Ir–C(1) = 177.8(2), Ir–C(1)–O(1) = 178.7(5), P(1)–Ir–C(1) = 93.0(1), P(1)–Ir–N(1) = 84.9(1), Ir–N(1)–C(76) = 130.4(3).

Of the three complexes, only *trans*-Ir(CO)[NH(*p*-C_6H_4-Me)]$(PPh_3)_2$ produced crystals suitable for single-crystal structural analysis. The complex crystallizes in the centrosymmetric triclinic system $P\bar{1}$. A ball-and-stick view of the molecule is shown in Figure 1. The Ir–N(1) distance of 2.041(3) Å is virtually identical with the Ir–O distance observed in *trans*-Ir(OPh)(CO)$(PPh_3)_2$.[13f] The remaining metal–ligand distances are also quite similar in the two complexes. The coordination geometry around the metal atom is virtually planar, and the bond distances and angles in the two phosphine ligands are normal. The plane of the amido phenyl ring is nearly perpendicular to the square plane around Ir and is also collinear with the N(1)–Ir(1)–C(1) vector. This particular conformation of the phenyl ring provides the sterically most favorable arrangement with respect to the phenyl rings of the two trans PPh_3 groups.

Interest in the study of late-transition-metal amido complexes stems, in part, from the expectation that the amido moiety in these complexes would act as a reactive functionality toward various substrates. We are examining many such reactions. Here, we describe the preliminary results of reactions involving insertion of CO and CO_2 into the Ir–amide bonds of 1 and 2, which are still considered to be rare for late transition metals.[14,15]

The amido complex 2 reacts readily with CO_2 at room

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(8) Anal. Calcd (found) for 1: C, 61.70 (61.22); H, 4.33 (4.46); N, 1.67 (1.65). Cacld (found) for 2: C, 62.09 (61.72); H, 4.50 (4.71); N, 1.64 (1.44); Calcd (found) for 3: C, 62.48 (62.75); H, 4.66 (4.74); N, 1.61 (1.47). IR data (CH_2Cl_2, ν(CO) in cm^{-1}): 1, 1944; 2, 1942; 3, 1940. ^1H NMR data (C_6D_6, δ relative to TMS): 1, 7.89, 6.96 (m, 30H, $P(C_6H_5)_3$), 6.74, 6.35 (m, 5H, $NH(C_6H_5)$), 2.62 (s, 1H, $NH(C_6H_5)$); 2, 7.89, 6.98 (m, 30H, $P(C_6H_5)_3$), 6.54, 6.34 (d, 4H, $NH(C_6H_4Me)$), 2.67 (s, 1H, $NH(C_6H_4Me)$), 2.12 (s, 3H, $NH(C_6H_4Me)$); 3, 7.82, 6.99 (m, 30H, $P(C_6H_5)_3$), 6.82 (d, 2H, $NH(C_6H_3Me_2)$), 6.29 (t, 1H, $NH(C_6H_3Me_2)$), 2.10 (s, 6H, $NH(C_6H_3Me_2)$), 1.81 (s, 1H, $NH(C_6H_3Me_2)$. $^{31}P\{^1H\}$ NMR data (δ relative to H_3PO_4): 1, 24.8; 2, 24.5; 3, 23.2.

(9) Crystallographic data for $C_{44}H_{38}NOP_2Ir\cdot{}^1/_2C_7H_8$: M_r = 897.0, triclinic, $P\bar{1}$ (No. 2), a = 9.217(2) Å, b = 11.778(2) Å, c = 19.798(4) Å, α = 90.89(3)°, β = 101.46(3)°, γ = 106.04(3)°, V = 2018.7(7) $Å^3$, Z = 2, D_{exptl} = 1.475 g cm^{-3}, μ = 34.20 cm^{-1}. Data were collected on a Siemens P4 diffractometer with graphite monochromator, λ(Mo Kα) = 0.710 73 Å, ω scans, $4° < 2\theta < 60°$, 17 660 reflections collected with 11 759 independent and 9451 observed ($F_o > 5.0\sigma(F_o)$]. On the basis of azimuthal scans which showed less than 10% variation, it was determined that no correction for absorption was required. The centrosymmetric space group was suggested by the distribution of E values and confirmed by the results of refinement. The Ir atom was obtained from a Patterson map. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were treated as idealized contributions. An end-for-end disordered molecule of toluene is located on the crystallographic inversion center. $R(F)$ = 4.14% (5.50% for all data), and $R(wF)$ = 4.77%. All software and the sources of the scattering factors are contained in the SHELXTL PLUS (Version 4.21, 1990) program library (G. Sheldrick, Siemens XRD, Madison, WI).

(10) Poulton, J. T.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 3190.

(11) Launder, D. M.; Lobkovsky, E. B.; Streib, W. E.; Caulton, K. G. *J. Am. Chem. Soc.* **1991**, *113*, 1837.

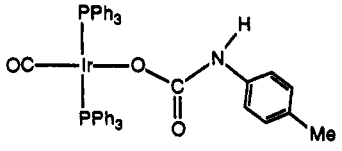
(12) Johnson, T. J.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1992**, *114*, 2725.

(13) (a) Bernard, K. A.; Atwood, J. D. *Organometallics* **1989**, *8*, 795; **1988**, *7*, 235; **1987**, *6*, 1133. (b) Bernard, K. A.; Churchill, M. R.; Janik, T. S.; Atwood, J. D. *Organometallics* **1990**, *9*, 12. (c) Thompson, J. S.; Bernard, K. A.; Rappoli, B. J.; Atwood, J. D. *Organometallics* **1990**, *9*, 2727. (d) Rappoli, B. J.; Janik, T. S.; Churchill, M. R.; Thompson, J. S.; Atwood, J. D. *J. Organomet. Chem.* **1988**, *7*, 1939. (e) Janik, T. S.; Bernard, K. A.; Churchill, M. R.; Atwood, J. D. *J. Organomet. Chem.* **1987**, *323*, 247. (f) Rees, W. M.; Churchill, M. R.; Fettinger, J. C.; Atwood, J. D. *Organometallics* **1985**, *4*, 2179.

(14) Insertion of CO_2 into the late-transition-metal–amide/imide bond: (a) Cowan, R. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4750. (b) Hartwig, J. F.; Bergman, R. G.; Anderson, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 6499. (c) Glueck, D. S.; Wu, J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 2041. Similar insertion reactions for early-transition-metal amides are reviewed in: Chisholm, M. H.; Rothwell, I. P. *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, England, 1987; Vol. 2, p 161.

(15) Insertion of CO into the late-transition-metal–amide/imide bond: (a) Reference 14c. (b) Bryndza, H. E.; Fultz, W. C.; Tam, W. *Organometallics* **1985**, *4*, 939. (c) Ge, Y.; Sharp, P. R. *Organometallics* **1988**, *7*, 2234 and references therein.

temperature. IR and NMR spectral data[16] suggest that insertion of CO_2 into the Ir–N bond has occurred to produce a carbamate complex of the type



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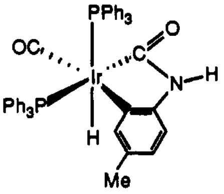
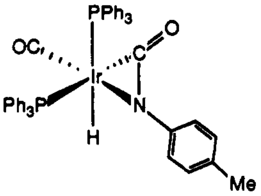
Complexes 1 and 2 also undergo a rapid reaction with CO. The addition of 1 equiv of CO at room temperature produces a major product in ~90% yield as evidenced by IR spectroscopy. The ^{1}H NMR spectrum[16,17] of 5 (product of the reaction between 2 and CO) in C_6D_6 shows a hydride resonance centered at δ −9.12. The 2200–1500-cm^{-1} region of its IR spectrum displays a weak broad band at 2093 cm^{-1}, assigned to the Ir–H stretching vibration, a strong band at 2016 cm^{-1}, assigned to the terminal CO ligand, and another strong band at 1598 cm^{-1}, indicative of a IrC(O)N═ type moiety. The use of 99 atom % ^{13}CO in the reaction shows isotopic enrichment for both the terminal CO and the –C(O)N═ ligands. On the basis of this spectroscopic evidence, we assign structure **5a** to complex 5. Another possibility would be the hydridophenyl isocyanate complex **5b**, although labeling studies utilizing $Ir(CO)(NHC_6D_5)(PPh_3)_2$ are strongly in favor of **5a**.



5a



5b

Complete characterization of the CO insertion products by means of labeling studies and NMR experiments is currently underway. Future studies will involve addition reactions of the new arylamido complexes with alkenes and alkynes.

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Supplementary Material Available: Tables giving a structural report of X-ray data collection and refinement, atomic coordinates of non-hydrogen atoms, all bond lengths and angles, anisotropic thermal parameters of non-hydrogen atoms, and hydrogen atom parameters and figures giving IR and ^{1}H and ^{31}P NMR spectra for 5 (11 pages). Ordering information is given on any current masthead page.

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(16) 4: IR in the carbonyl region (CH_2Cl_2, cm^{-1}) 1959 (s, Ir–CO), 1501 (m, IrO(C═O)–); ^{1}H NMR (C_6D_6) δ 2.10 (s, 3H, C*H*$_3$), 5.56 (br s, 1H, N*H*), 6.79–8.00 (multiplets, 34H, phenyl H); ^{13}C NMR ($CDCl_3$) of a $^{13}CO_2$-labeled sample δ 157.2. 5: ^{1}H NMR (C_6D_6) δ −9.12 (d of d, 1H, J_{P-H} = 127 and 19 Hz, Ir–*H*), 2.10 (s, 3H, C*H*$_3$), 6.20–7.75 (multiplets, 33H, phenyl H), 8.02 (s, 1H, N*H*); ^{31}P{^{1}H} NMR (C_6D_6) δ 0.1 and 5.2 (d, J_{P-P} = 18 Hz); ^{13}C NMR (C_6D_6) of ^{13}CO-enriched sample δ 190.9 (multiplet, Ir–*C*O), 178.9 (multiplet, Ir*C*(O)N═).

(17) ^{1}H, ^{13}P{^{1}H}, and IR spectra of 5 have been submitted as supplementary material.