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Iridium(I) Complexes of π-Acidic Carboxamides

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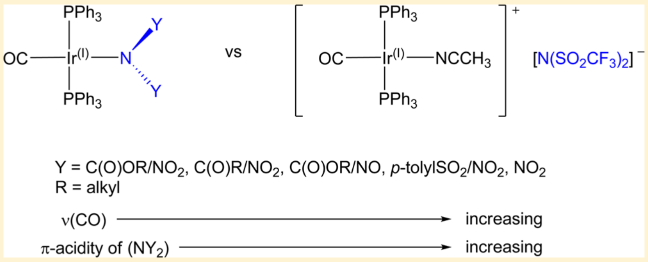
Supporting Information

ABSTRACT: The silver salts of the conjugate bases of the nitrogen acids *N*-nitroacetamide ($Ag[CH_3C(O)NNO_2]$ (**1**)), *N*-nitrocarbamate ($Ag[R'OC(O)NNO_2]$, R′ = CH_3 (**2**), C_2H_5 (**3**)), *N*-nitrosomethylcarbamate ($Ag[CH_3OC(O)NNO]$ (**4**)), and *N*-nitro-*p*-tolylsulfonamide, ($Ag[p\text{-tolylSO}_2NNO_2]$ (**5**)) react with *trans*-$Ir(Cl)(CO)(PPh_3)_2$ (Vaska's complex) to give *trans*-$Ir(\eta^1$-nitrogen acid$)(CO)(PPh_3)_2$ complexes (**6**−**10**). The related silver amides dinitramide and bistriflimide also react with *trans*-$Ir(Cl)(CO)(PPh_3)_2$, to give *trans*-$Ir[\eta^1\text{-}N(NO_2)_2](CO)(PPh_3)_2$ (**11**) and the unusual silver adduct [*trans*-$Ir(Cl)(CO)(PPh_3)_2][Ag[N(SO_2CF_3)_2]]$ (**12**), respectively. The reaction of trimethylsilyl bistriflimide, prepared in situ from trimethylsilyl bromide and $Ag[N(SO_2CF_3)_2]$ in acetonitrile, and $Ir(F)(CO)(PPh_3)_2$ gives [*trans*-$Ir(CH_3CN)(CO)(PPh_3)_2][N(SO_2CF_3)_3]$ (**13**). The molecular structures of these complexes are all square planar, with the exception of **12**, which is square pyramidal with the AgX ligand in the apical position. Complexes **6**−**9**, **12**, and **13** are stable to air in solution, while **10** and **11** are reactive toward oxygen.



INTRODUCTION

One of the unifying themes of transition-metal organometallic chemistry is not only the marked covalency of metal−element single bonds but also their frequent covalent double-bond character. π bonds to carbon-bound donor ligands are now well established and have led to many of the key developments in organometallic chemistry in the last 70 years. With the exception of the metallo-nitrosyl, -nitrides, and -imides, which also have strong covalent and π bonding, the π-acidic nitrogen donor ligands as a class are much less well developed and possibly rare, with most examples of M−N bonding being due to π bases. Given that many of the nitrogen π acids such as nitrosyls exhibit tunable amphoteric character in the π interactions, we seek to extend the members of this family to other nitrogen donor ligands.

The nitrogen acids *N*-nitroamide ($RC(O)NHNO_2$, R = CH_3 (**1**), C_2H_5 (**2**)), *N*-nitrocarbamate ($R'OC(O)NHNO_2$, R′ = CH_3 (**3**), C_2H_5 (**4**)), and *N*-nitrosocarbamate are a class of primary carboxamide compounds that contain N-bound electronegative functional groups $-NO_2$ and $-NO$. This class of unusual carboxamides gives rise to different electronic and spectroscopic properties in comparison to the numerous simple carboxamides.[1] To investigate the electronic properties of this class of compounds, derivative complexes of *trans*-$Ir(X)(CO)(PPh_3)_2$, where X = Cl is Vaska's complex and where X is the anionic ligand of the conjugate base of the nitrogen acids, can allow us to better understand how these ligands bind to low-valent metal centers. This strategy of deriving electronic properties of ligands to transition-metal complexes using Vaska's complex is well established with considerable precedent.[2] Another approach to directly measure the acidity of these nitrogen acids might be that formulated by Stayanov.[3] In this report the focus is on the nature of ligand−metal interaction, in particular the π-back-bonding ability of these ligands. For these considerations more than a simple pK_a is required, and thus we use competitive π back-donation.

For comparison with these new anionic nitrogen acid ligands, Vaska's complex derivatives containing amides such as dinitramide ($[N(NO_2)]^-$) and bistriflimide ($[N(SO_2CF_3)_2]^-$), which contain the nitro and trifluoromethanesulfonyl functional groups, have also been prepared and characterized. We find these electron-withdrawing anions are good electron acceptors which modulate the electronic structure and reactivity of the metal center. The square-planar geometry and strictly trans relationship of the carbonyl and anion ligands ensure that the observed changes are only marginally affected by steric interactions.

EXPERIMENTAL SECTION

Except as noted, reagents and solvents were used as supplied commercially. Dry CH_3OH was distilled from freshly generated magnesium methoxide, dry $CHCl_3$ was distilled from $CaCl_2$, dry CH_2Cl_2 and CH_3CN were distilled from CaH_2, and dry hexanes, pentanes, toluene, and benzene were distilled from sodium benzophenone ketyl. The IR spectra were recorded in KBr or Nujol matrix using an ABB Bomem MB Series IR spectrometer with a spectral resolution of 4 cm^{-1}. Decomposition/melting points were measured by using a TA-Q2000 differential scanning calorimeter calibrated against an internal standard. Elemental analyses were performed in the Elemental Analyses Laboratory at the University of Montreal. The syntheses of the free *N*-nitro nitrogen acids have been reported in prior work and the literature.[4] The synthesis of *N*-

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nitrosomethylcarbamate is described in the Supporting Information. $Li[N(SO_2CF_3)_2]$ was purchased from Acros Organics and used without purification. *trans*-$Ir(Cl)(CO)(PPh_3)_2$,[5] *trans*-$Ir(F)(CO)(PPh_3)_2$,[6] $NH_4[N(NO_2)_2]$,[7] $K[N(NO_2)_2]$,[8] $Ag[N(NO_2)_2]$,[9] and $H[N(SO_2CF_3)_2]$[10] were synthesized according to literature procedures. $Ag[N(SO_2CF_3)_2]$[11] was synthesized from Ag_2CO_3 instead of Ag_2O. The following reactions were carried out under strict exclusion of light, due to the light sensitivity of the silver salts.

X-ray Crystallography. Crystals were mounted on glass fibers with epoxy resin or Mitegen mounts using Paratone-N from Hampton Research, and single-crystal X-ray diffraction experiments were carried out with a Bruker SMART CCD or Bruker APEX-II CCD diffractometer by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and Kryoflex for low-temperature experiments. SAINT[12] was used for integration of the intensity reflections and scaling and SADABS[13] for absorption correction. Direct methods or Patterson maps were used to generate the initial solutions. Non-hydrogen atoms were located by difference Fourier maps, and final solution refinements were solved by full-matrix least-squares methods on F^2 of all data, by using SHELXTL[12] software. The hydrogen atoms were placed in calculated positions. SHELXTL restraints such as ISOR, SIMU, DELU, and SADI were applied to a disordered solvent molecule for **9** and for the disordered bistriflimide anion in **13**.

Crystals of **6**−**8** and **10**−**12** were grown from CH_2Cl_2/CH_3OH layered solutions at −21 °C, **9** from diffusion of pentanes into CH_2Cl_2/THF, and **13** from C_2H_5OH. Crystallographic data and data collection parameters for the nitrogen acids and Ir(I) complexes are shown in Table S1 (Supporting Information).

Silver *N*-Nitroacetamide, $Ag[CH_3C(O)NNO_2]$ (1). *N*-Nitroacetamide[4a] (0.108 g, 1.04 mmol) was dissolved in CH_2Cl_2 (6 mL), Ag_2CO_3 (0.143 g, 0.518 mmol) was added, and the mixture was stirred overnight at room temperature. The white suspension was filtered, washed with minimum CH_2Cl_2, and dried to give white solids of $Ag[CH_3C(O)NNO_2]$ (**1**) (0.210 g, 0.996 mmol, 96% yield). IR (KBr; cm^{-1}): 1977 vw, 1642 vs, 1504 w, 1427s , 1364 s, 1304 s, 1222 vs, 1048 m, 1037 m, 992 s, 934 m, 797 m, 766 m, 623 m, 477 w. IR (Nujol; cm^{-1}): 2725 vw, 2669 vw, 1575 m, 1561 m, 1534 m, 1404w, 1312 m, 1235 m, 1208 m, 1105w, 1056w, 1029 m, 887 m, 769 m, 722 m, 632 m, 587 w. Anal. Calcd for $C_2H_3N_2O_3Ag$ (210.93 g mol^{-1}): C, 11.37; H, 1.42; N, 13.27. Found: C, 11.47; H, 1.31; N, 12.97.

Silver *N*-Nitromethylcarbamate, $Ag[CH_3OC(O)NNO_2]$ (2). *N*-Nitromethylcarbamate[4a] (0.045 g, 0.375 mmol) was dissolved in CH_2Cl_2 (5 mL), Ag_2CO_3 (0.050 g, 0.181 mmol) was added, and the mixture was stirred overnight at room temperature. The white suspension was filtered and the residue washed with CH_2Cl_2 and dried to give white solids of $Ag[CH_3OC(O)NNO_2]$ (**2**) (0.060 g, 0.265 mmol, 73% yield). IR (KBr; cm^{-1}): 3020 vw, 2965w, 1683 vs, 1453 m, 1405 s, 1312 m, 1236 s, 1191 s, 1106 s, 963 w, 806 w, 783 m, 739 w, 430 w. IR (Nujol; cm^{-1}): 2724 vw, 1712 m, 1702 m, 1687 m, 1643 m, 1314 m, 1246 m, 1187 m, 1125 m, 1114 m, 944 m, 797 w, 767 m, 722 m, 664 w, 600 w, 548 vw. IR (Nujol; cm^{-1}): 2723 vw, 2674 vw, 1698 m, 1664 vs, 1421 vs, 1242 vs, 1127s, 1110s, 1023 m, 992 m, 886 m, 821 w, 768 m, 722 w, 455 w. Anal. Calcd for $C_2H_3N_2O_4Ag$ (226.93 g mol^{-1}): C, 10.57; H, 1.32; N, 12.33. Found: C, 10.50; H, 1.28; N, 12.17.

Silver *N*-Nitroethylcarbamate, $Ag[C_2H_5OC(O)NNO_2]$ (3). *N*-Nitroethylcarbamate[4a] (0.200 g, 1.49 mmol) was dissolved in CH_2Cl_2 (5 mL), Ag_2CO_3 (0.200 g, 0.726 mmol) was added, and the mixture was stirred overnight at room temperature. The white suspension was filtered and the residue washed with CH_2Cl_2 and dried to give white solids of $Ag[C_2H_5OC(O)NNO_2]$ (**3**) (0.258 g, 1.07 mmol, 74% yield). The IR spectroscopic details are identical with those in the literature.[14] IR (KBr; cm^{-1}): 2990 w, 1696 s, 1668 m, 1488 w, 1474 w, 1405 m, 1369 w, 1314 m, 1241 vs, 1127 m, 1097 s, 1033 w, 994 w, 886 w, 769 w, 487 w. IR (Nujol; cm^{-1}): 2723 vw, 2674 vw, 1698 m, 1664 s, 1421s, 1299 m, 1242 vs, 1127 s, 1110 m, 1023 m, 992 m, 886 m, 821 w, 768 m, 722 w, 455 w. Anal. Calcd for $C_3H_5N_2O_4Ag$ (240.95 g mol^{-1}): C, 14.94; H, 2.08; N, 11.62. Found: C, 15.07; H, 1.99; N, 11.60.

Silver *N*-Nitrosomethylcarbamate, $Ag[CH_3OC(O)NNO]$ (4). An isomeric mixture of *N*-nitrosomethylcarbamate was synthesized using procedures for *N*-nitrosoethylcarbamate but with modifications (Supporting Information).

N-Nitrosomethylcarbamate (0.040 g, 0.385 mmol) was dissolved in dry CH_2Cl_2 (4 mL), and Ag_2CO_3 (0.052 g, 0.189 mmol) was added. The suspension was stirred overnight to give a yellow suspension. The solvent of the suspension was removed under vacuum to remove any unreacted starting nitrosocarbamate, to give yellow solids of $Ag[CH_3OC(O)NNO]$ (**4**) (0.065 g, 0.308 mmol, 82% yield). *Caution! The yellow solids are sensitive to friction and can detonate!* It is best to resuspend the yellow solids in CH_2Cl_2 before transferring to a sample vial followed by removal of the solvent under vacuum. IR (KBr; cm^{-1}): 2958 w, 1697 s, 1441 m, 1211 vs, 1072 s, 960 w, 798 m, 465 w. IR (Nujol; cm^{-1}): 2723 vw, 1690 m, 1428 m, 1266 s, 1236 s, 1190 m, 1099 m, 955 m, 803 e, 784 m, 722w, 664 vw, 601 vw, 465 m. Anal. Calcd for $C_2H_3N_2O_3Ag$ (210.96 g mol^{-1}): C, 11.39; H, 1.43; N, 13.28. Found: C, 12.11; H, 1.63; N, 13.17.[15] These elemental analyses are a significant improvement on a prior report and reflect the thermal instability of these salts.[15]

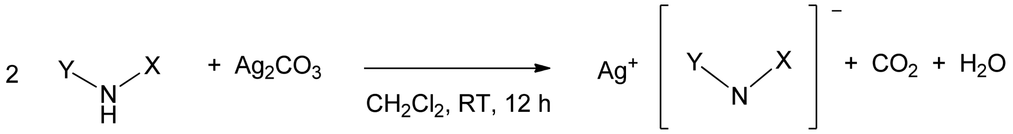
Silver *N*-Nitro-*p*-tolylsulfonamide, $Ag[p\text{-}C_7H_7SO_2NNO_2]$ (5). *N*-Nitro-*p*-tolylsulfonamide[4b] (0.315 g, 1.46 mmol) was dissolved in CH_2Cl_2 (5 mL), Ag_2CO_3 (0.200 g, 0.726 mmol) was added, and the mixture was stirred overnight at room temperature. The white suspension was filtered and the residue washed with CH_2Cl_2 and dried to give white solids of $Ag[p\text{-}C_7H_7SO_2NNO_2]$ (**5**) (0.318 g, 0.986 mmol, 68% yield). IR (KBr; cm^{-1}): 3045 vw, 2920 vw, 1596 w, 1435 s, 1382 m, 1301 vs, 1286 vs, 1151 s, 1140 s, 1078 m, 1044 m, 1018 w, 909 w, 870 w, 815 w, 774 w, 755 w, 666 s, 600 s, 543 m. IR (Nujol; cm^{-1}): 2725 vw, 2673 vw, 1641w, 1590 vw, 1291 m, 1265 m, 1131 m, 1072 m, 1031 m, 911 m, 813 w, 774 w, 722 w, 666 m, 595 m, 547 w, 492 w. Anal. Calcd for $C_7H_7N_2O_4SAg$ (323.08 g mol^{-1}): C, 25.99; H, 2.17; N, 8.67; S, 9.90. Found: C, 26.13; H, 2.11; N, 8.65; S, 10.21.

$Ir(\eta^1\text{-}CH_3C(O)NNO_2)(CO)(PPh_3)_2$ (6). *trans*-$Ir(Cl)(CO)(PPh_3)_2$ (0.080 g, 0.103 mmol) was dissolved in degassed $CHCl_3$ (5 mL) under an N_2 atmosphere. Compound **1** (0.022 g, 0.104 mmol) was added, and the mixture was stirred for 2 h at room temperature. A white precipitate was formed and was filtered through a Celite plug to give a yellow solution. The solvent was removed in vacuo, and the yellow residue was recrystallized from CH_2Cl_2/CH_3OH to give yellow crystals of $Ir(\eta^1\text{-}CH_3C(O)NNO_2)(CO)(PPh_3)_2$ (**6**) (0.065 g, 0.0767 mmol, 75% yield). IR (KBr; cm^{-1}): 3077 vw, 3053 vw, 1968 vs (CO), 1652 m, 1491 m, 1436 m, 1224 m, 1097 m, 1027 w, 747 m, 694 m, 521 m. Raman (cm^{-1}): 3065 vw, 1970 vw, 1591 m, 1576 vw, 1192 vw, 1100 m, 1030 m, 1002 vs, 618 m, 571 m, 255 w. ^1H NMR (200 MHz, $CDCl_3$) ppm: δ 1.23 (s, 3H), 7.42 (m, PPh_3), 7.73 (m, PPh_3). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) ppm: δ 26.76 (s). ESI-MS: 849.16 $[M]^+$. Decomposition point: 179.3 °C (195.1 kJ mol^{-1}). Anal. Calcd for $C_{39}H_{33}N_2O_4P_2Ir{\cdot}0.9CH_2Cl_2$ (924.31 g mol^{-1}): C, 51.85; H, 3.79; N, 3.03. Found: C, 52.37; H, 3.22; N, 3.06.

$Ir(\eta^1\text{-}CH_3OC(O)NNO_2)(CO)(PPh_3)_2$ (7). *trans*-$Ir(Cl)(CO)(PPh_3)_2$ (0.030 g, 0.0385 mmol) was dissolved in degassed $CHCl_3$ (5 mL) under an N_2 atmosphere. Compound **2** (0.009 g, 0.0397 mmol) was added, and the mixture was stirred for 3 h at room temperature. A brown precipitate was formed and was filtered through a Celite plug to give a yellow solution. The solvent was removed in vacuo, and the yellow residue was recrystallized from CH_2Cl_2/CH_3OH to give yellow crystals of $Ir(\eta^1\text{-}CH_3OC(O)NNO_2)(CO)(PPh_3)_2$ (**7**) (0.025 g, 0.0292 mmol, 76% yield). IR (KBr; cm^{-1}): 3055 w, 2921 w, 2851 w, 1965 vs (CO), 1875 w, 1739 s, 1683 w, 1482 m, 1435s, 1315 w, 1230 m, 1204 s, 1181 s, 1160 m, 1096 s, 1027 w, 999 w, 745 m, 694 vs, 611 w, 521 vs, 499 m. ^1H NMR ($CDCl_3$) ppm: δ 7.68 (m, PPh_3), 7.43 (m, PPh_3), 3.08 (s, 3H). $^{31}P\{^1H\}$ NMR ($CDCl_3$) ppm: δ 25.03 (s). Decomposition point: 206.4 °C (228.6 kJ mol^{-1}). Anal. Calcd for $C_{39}H_{33}N_2O_5P_2Ir$ (863.86 g mol^{-1}): C, 54.17; H, 3.82; N, 3.24. Found: C, 54.19; H, 3.91; N, 3.13.

$Ir(\eta^1\text{-}C_2H_5OC(O)NNO_2)(CO)(PPh_3)_2$ (8). *trans*-$Ir(Cl)(CO)(PPh_3)_2$ (0.100 g, 0.128 mmol) was dissolved in degassed $CHCl_3$ (10 mL) under an N_2 atmosphere. Compound **3** (0.037 g, 0.154 mmol) was added, and the mixture was stirred for 3 h at room temperature. A

Scheme 1. Synthesis of Silver Salts of *N*-Nitroamides, *N*-Nitrocarbamates, *N*-Nitrosocarbamates, and *N*-Nitro-*p*-tolylsulfonamides



Y	X	Compound
$CH_3C(O)$	NO_2	**1**
$CH_3OC(O)$	NO_2	**2**
$C_2H_5OC(O)$	NO_2	**3**
$CH_3OC(O)$	NO	**4**
p-tolylSO_2	NO_2	**5**

brown precipitate was formed and was filtered through a Celite plug to give a yellow solution. The solvent was removed in vacuo, and the yellow residue was recrystallized from CH_2Cl_2/CH_3OH to give yellow crystals of Ir(η^1-$C_2H_5OC(O)NNO_2$)(CO)(PPh_3)$_2$ (**8**) (0.100 g, 0.113 mmol, 88% yield). IR (KBr; cm^{-1}): 3055 w, 2981 vw, 2900 vw, 1959 vs (CO), 1912 w, 1731 s, 1688 w, 1587 w, 1572 w, 1492 m, 1481 m, 1435 s, 1388 w, 1365 w, 1292 w, 1202 s, 1185 m, 1163 m, 1096 s, 1029 w, 998 m, 882 w, 769 w, 759 m, 745 m, 706 m, 693 w, 614 m, 518 s, 499 m. ^{1}H NMR (200 MHz, $CDCl_3$) ppm: δ 0.99 (t, 3H, J = 7.1 Hz), 3.47 (q, 2H, J = 7.1 Hz), 7.43 (m, PPh_3), 7.72 (m, PPh_3). ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) ppm: δ 26.22 (s). ESI-MS: 900.84 [M + Na]$^+$. Decomposition point: 213.3 °C (179.6 kJ mol^{-1}). Anal. Calcd for $C_{40}H_{35}N_2O_4P_2Ir$ (877.88 g mol^{-1}): C, 54.67; H, 3.99; N, 3.19. Found: C, 54.45; H, 3.89; N, 3.13.

Ir(η^1-$CH_3OC(O)NNO$)(CO)(PPh_3)$_2$ (9). *trans*-Ir(Cl)(CO)(PPh_3)$_2$ (0.060 g, 0.0770 mmol) and **4** (0.018 g, 0.0854 mmol) were placed together in a reaction flask. Dry and degassed $CHCl_3$ (6 mL) was added under an N_2 atmosphere, and the mixture was stirred for 3 h at room temperature in an inert-atmosphere glovebox. A white precipitate was formed and was filtered through a Celite plug to give a bright yellow solution. The solvent was removed in vacuo, and the yellow residue was recrystallized from dry and degassed CH_2Cl_2/pentanes to give yellow solids of Ir(η^1-$CH_3OC(O)NNO$)(CO)(PPh_3)$_2$ (**9**) (0.056 g, 0.0662 mmol, 86% yield). IR (KBr; cm^{-1}): 3055 vw, 2949 vw, 2841 vw, 1968 vs (CO), 1734 w, 1702 m, 1636 w, 1480 m, 1436 m, 1400 m, 1323 m, 1262 w, 1235 w, 1185 w, 1147 m, 1093 s, 1028 w, 998 w, 777 w, 747 m, 694 m, 610 m, 522 s, 513 m, 498 m. ^{1}H NMR (200 MHz, $CDCl_3$) ppm: δ 3.23 (s, 3H), 7.41 (m, PPh_3), 7.70 (m, PPh_3). ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) ppm: δ 25.86 (s). Decomposition point: 151.6 °C (159.0 kJ mol^{-1}). Anal. Calcd for $C_{39}H_{33}N_2O_4P_2Ir$ (847.86 g mol^{-1}): C, 55.19; H, 3.89; N, 3.30. Found: C, 55.04; H, 3.77; N, 3.43.

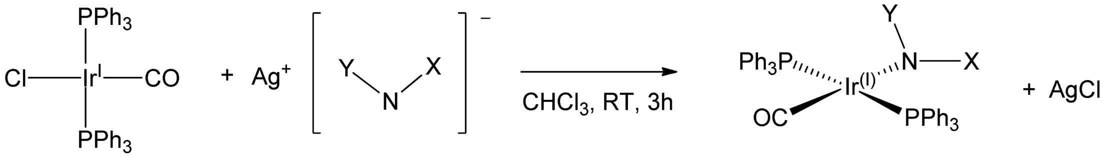
Ir(η^1-$C_7H_7SO_2NNO_2$)(CO)(PPh_3)$_2$ (10). *trans*-Ir(Cl)(CO)(PPh_3)$_2$ (0.030 g, 0.0385 mmol) and **5** (0.013 g, 0.0403 mmol) were placed together in a reaction flask. Dry and degassed $CHCl_3$ (5 mL) was added under an N_2 atmosphere, and the mixture was stirred for 3 h at room temperature in an inert-atmosphere glovebox. A white precipitate was formed and was filtered through a Celite plug to give a bright yellow solution. The solvent was removed in vacuo, and the yellow residue was recrystallized from dry and degassed CH_2Cl_2/CH_3OH to give yellow solids of Ir(η^1-$C_7H_7SO_2NNO_2$)(CO)(PPh_3)$_2$ (**10**) (0.025 g, 0.0257 mmol, 67% yield). IR (KBr; cm^{-1}): 3054 vw, 2961 vw, 2919 vw, 2847 vw, 1977 vs (CO), 1596 w, 1493 s, 1482 m, 1434 s, 1339 m, 1275 m, 1154 s, 1093 s, 1013 m, 922 m, 812 m, 744 m, 693 s, 661 m, 605 w, 589 s, 542 m, 516 vs, 495 m, 452 w. ^{1}H NMR (200 MHz, $CDCl_3$) ppm: δ 2.28 (s, 3H), 6.82 (d, 2H, J = 8 Hz), 7.39 (m, p-tolyl and PPh_3), 7.64 (m, PPh_3). ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) ppm: δ 24.60 (s). Decomposition point: 192.4 °C (182.4 kJ mol^{-1}). Anal. Calcd for $C_{44}H_{37}N_2O_5P_2SIr\cdot 0.75CH_2Cl_2$ (1023.72 g mol^{-1}): C, 52.50; H, 3.79; N, 2.74; S, 3.13. Found: C, 52.84; H, 3.92; N, 2.60; S, 2.76.

Ir[η^1-$N(NO_2)_2$](CO)(PPh_3)$_2$ (11). *trans*-Ir(Cl)(CO)(PPh_3)$_2$ (0.030 g, 0.0385 mmol) was dissolved in dry and degassed $CHCl_3$ (5 mL) and added to a dry CH_3CN (2 mL) solution containing Ag[$N(NO_2)_2$] (0.010 g, 0.0421 mmol). A white precipitate appeared immediately, and this was stirred overnight at room temperature under a N_2 atmosphere in an inert-atmosphere glovebox. The suspension was filtered through a Celite plug to give a bright yellow solution. The solvent was removed in vacuo, and the yellow oil was recrystallized from dry and degassed CH_2Cl_2/CH_3OH to give brown crystals of Ir(η^1-$N(NO_2)_2$)(CO)(PPh_3)$_2$ (**11**) (0.0036 g, 0.0424 mmol, 11% yield) contaminated with large (significant) amounts of yellow crystals of *trans*-Ir(Cl)(CO)(PPh_3)$_2$. IR (KBr; cm^{-1}): 3054 vw, 2962 vw, 2924 vw, 2068 w, 2024 vw, 1981 vs (CO), 1633 w, 1588 w, 1567 s, 1480 m, 1435 s, 1385 w, 1309 w, 1264 w, 1193 s, 1158 m, 1095 s, 1057 w, 998 w, 967 m, 827 w, 746 m, 693 s, 607 m, 521 s, 514 s, 500 m, 423 w. ^{1}H NMR (200 MHz, $CDCl_3$) ppm: δ 7.55 (m, PPh_3), 7.68 (m, PPh_3). ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) ppm: δ 25.40.

Ir(Cl)(CO)(PPh_3)$_2$[Ag($N(SO_2CF_3)_2$)] (12). *trans*-Ir(Cl)(CO)(PPh_3)$_2$ (0.030 g, 0.0385 mmol) was dissolved in dry and degassed $CHCl_3$ (5 mL) and added to a dry CH_3CN (2 mL) solution containing Ag[$N(SO_2CF_3)_2$] (0.0156 g, 0.400 mmol). A white precipitate appeared immediately (most likely some insoluble silver salt) and was stirred overnight at room temperature under a N_2 atmosphere in an inert-atmosphere glovebox. The suspension was filtered through a Celite plug to give a bright yellow solution. The solvent was removed in vacuo, and the yellow oil was recrystallized from dry and degassed CH_2Cl_2/CH_3OH to give yellow crystals of Ir(Cl)(CO)(PPh_3)$_2$[Ag($N(SO_2CF_3)_2$)] (**12**) (0.017 g, 0.0146 mmol, 38% yield) contaminated with small amounts of yellow crystals of *trans*-Ir(Cl)(CO)(PPh_3)$_2$. IR (KBr; cm^{-1}): 3058 w, 2963 w, 2918 w, 2012 s (CO), 1986 m (CO), 1957 w, 1627 w, 1481 w, 1436 m, 1390 m, 1356 s, 1262 m, 1197 s, 1133 s, 1096 vs, 1063 m, 1026 m, 997 s, 805 m, 747 m, 693 m, 613 m, 569 w, 513 s, 461 w. ^{1}H NMR (200 MHz, $CDCl_3$) ppm: δ 7.43 (m, 18H, PPh_3), 7.68 (m, 12H, PPh_3). ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) ppm: δ 23.82 (s). Anal. Calcd for $C_{39}H_{30}NO_5F_6P_2S_2ClAgIr$ (1168.27 g mol^{-1}): C, 40.05; H, 2.57; N, 1.20; S, 5.48. Found: C, 40.32; H, 2.63; N, 1.18; S, 5.21.

[*trans*-Ir(CH_3CN)(CO)(PPh_3)$_2$][$N(SO_2CF_3)_2$] (13). Trimethylsilyl bromide (TMSBr; 9.5 μL, 0.072 mmol) was added to a suspension containing Ag[$N(SO_2CF_3)_2$] (0.030 g, 0.077 mmol) in a mixture of dry and degassed CH_2Cl_2/CH_3CN (10 mL) at 0 °C under N_2. An off-white precipitate (AgBr) was observed to form immediately, and the reaction mixture was stirred for 30 min. *trans*-Ir(F)(CO)(PPh_3)$_2$ (0.050 g, 0.066 mmol) was added to the suspension, and the mixture was stirred for 2 h under N_2, during which time the temperature was

Scheme 2. Synthesis of Ir(η^1-nitrogen acid)(CO)(PPh$_3$)$_2$



Y	X	Silver compound	Complex
$CH_3C(O)$	NO_2	**1**	**6**
$CH_3OC(O)$	NO_2	**2**	**7**
$C_2H_5OC(O)$	NO_2	**3**	**8**
$CH_3OC(O)$	NO	**4**	**9**
p-tolylSO_2	NO_2	**5**	**10**
NO_2	NO_2		**11**

raised to room temperature. The solvent was removed in vacuo, the residue was extracted with CH_2Cl_2, and the extract was filtered through a Celite pad. The solvent was removed and the yellow oil recrystallized from EtOH/pentanes with addition of a few drops of CH_3CN to give yellow crystals of [*trans*-Ir(CH_3CN)(CO)(PPh_3)$_2$]-[N(SO_2CF_3)$_2$] (**13**) (0.058 g, 0.054 mmol, 83% yield). IR (KBr; cm^{-1}): 3060 w, 2929 vw, 2359 vw, 2329 vw, 2296 vw, 1979 s (CO), 1642 m, 1481 m, 1436 m, 1347 s, 1332 m, 1229 m, 1196 vs, 1191 vs, 1135 s, 1096 s, 1061 s, 1027 m, 998 m, 788 w, 759 m, 745 m, 709 m, 694 s, 612 m, 570 m, 522 m. ^{1}H NMR (CD_2Cl_2) ppm: 1.46 (s, CH_3), 7.59 (m, 18H, PPh_3), 7.69 (m, 12H, PPh_3). ^{19}F NMR (CD_2Cl_2) ppm: δ −79.51 (s). ^{31}P{1H} NMR (200 MHz, CD_2Cl_2) ppm: δ 23.89 (s). Endothermic point: 178.7 °C (−30.6 kJ mol^{-1}). Anal. Calcd for $C_{39}H_{30}NO_5F_6P_2S_2Ir$ (1062.93 g mol^{-1}): C, 46.15; H, 3.10; N, 2.63; S, 6.00. Found: C, 45.92; H, 3.15; N, 2.19; S, 5.79.

***trans*-Ir[N(SO_2CF_3)$_2$](CO)(PPh_3)$_2$ (14).** Using a preparation similar to that for **12**, but without addition of CH_3CN, trimethylsilyl bromide (TMSBr) (6 μL, 0.043 mmol) was added to a suspension containing Ag[N(SO_2CF_3)$_2$] (0.019 g, 0.049 mmol) in a mixture of dry and degassed CH_2Cl_2 (10 mL) at 0 °C under N_2. An off-white precipitate (AgBr) was observed to form immediately, and the reaction mixture was stirred for 30 min. *trans*-Ir(F)(CO)(PPh_3)$_2$ (0.032 g, 0.042 mmol) was added to the suspension and stirred for 3 h under N_2, during which time the temperature was raised to room temperature. The de yellow suspension was filtered through a Celite pad and concentrated to ca. 1 mL followed by addition of dry pentanes to precipitate out vermilion solids of *trans*-Ir[N(SO_2CF_3)$_2$](CO)(PPh_3)$_2$ (**13**) (0.040 g, 0.039 mmol, 93% yield). IR (KBr; cm^{-1}): 3057 w, 2928 vw, 2055 w, 1992 s (CO), 1631 w, 1587 w, 1482 m, 1436 s, 1352 s, 1332s, 1228s, 1197 vs, 1135 vs, 1096 vs, 1058 vs, 1028 m, 998 m, 788 w, 745 m, 694 s, 614 m, 570 m, 521 s. ^{1}H NMR (CD_2Cl_2) ppm: 7.56 (m, PPh_3), 7.65 (m, PPh_3). ^{19}F NMR (CD_2Cl_2) ppm: δ −79.52 (s). ^{31}P{1H} NMR (200 MHz, CD_2Cl_2) ppm: δ 23.87 (s). Anal. Calcd for $C_{39}H_{30}NO_5F_6P_2S_2Ir$ (1024.95 g mol^{-1}): C, 45.70; H, 2.95; N, 1.37; S, 6.26. Found: C, 46.34; H, 3.24; N, 1.57; S, 5.33.

■ RESULTS AND DISCUSSION

Silver Salts of Nitrogen Acids. The silver salts for the *N*-nitro compounds were synthesized by reaction of the nitrogen acid with silver carbonate (Ag_2CO_3) (Scheme 1).

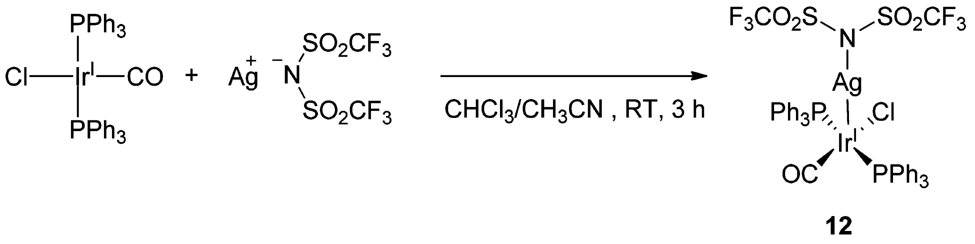
Heterogeneous suspensions of insoluble silver carbonate and the dissolved nitrogen acids in CH_2Cl_2 were stirred overnight in the absence of light to generate the corresponding insoluble silver salts in good yield. This is in contrast to the poor yields obtained for **3** when the reactions were carried out in water.[14] With the exception of **4**, all the silver salts are white solids which are thermally stable. The silver nitrosocarbamate **4** is a yellow friction-sensitive solid when dry. Isolation of **4** during the reduction of [NH_4][$CH_3OC(O)NNO_2$] can, however, be made safer by maintaining solvent moisture throughout its isolation and handling. *However, isolation of* ***4*** *as a solid from the above preparation requires special precautions, as detonation of the substance has occurred once on retrieval of the product from the sintered-glass frit due to friction!*

The vibrational spectra of the silver salts of the nitrogen acids are mostly similar between the Nujol and KBr matrixes, with the exception of **1** and **5**. However, close inspection of these spectra with those of the potassium salt indicate varying degrees of potassium substitution for silver in the KBr matrix.[16] Therefore, the Nujol spectra are a better representation of the silver salts. In general, there are several common strong bands. The first is the amide band 1 observed around 1575 cm^{-1} for **1** and 1700 cm^{-1} for the nitro/nitrosocarbamate salts. For the *N*-nitroamides/*N*-nitrocarbamates/*N*-nitrosulfonamides, the common strong bands are between 1400 and 1460 cm^{-1} and between 1220 and 1290 cm^{-1}, which most likely correspond to the asymmetric and symmetric stretches of the nitro group. Strong bands near the 900−1105 cm^{-1} region can mostly be assigned to the N−N stretch for the *N*-nitro/*N*-nitroso amides/carbamates. Additional bands between 1110 and 1200 cm^{-1} are also observed in the carbamate salts. Multiple bands of medium intensity are observed between 1300 and 1500 cm^{-1}, which are most likely due to the nitroso stretch. The IR spectrum of **3** is similar to that reported in the literature.[14]

The Ir(I) carbonyl complexes of the nitrogen acids and related amides were synthesized from the reaction of *trans*-Ir(Cl)(CO)(PPh_3)$_2$ and the corresponding silver salts (Scheme 2).

The new Ir(I) carbonyl complexes containing the nitrogen acids and related amides were obtained in good yields, except for **11**. Complex **11** was always obtained as a mixture of *trans*-Ir(Cl)(CO)(PPh_3)$_2$ and **11**, with the latter as a minor component. A significant amount of triphenylphosphine oxide was also observed in the ^{31}P NMR spectrum during the isolation process which indicates oxidation of the phosphine ligand of *trans*-Ir(Cl)(CO)(PPh_3)$_2$. There seems to be a competition between silver chloride formation and oxidation of

Scheme 3. Reaction of Silver Bistriflimide with *trans*-Ir(Cl)(CO)(PPh$_3$)$_2$



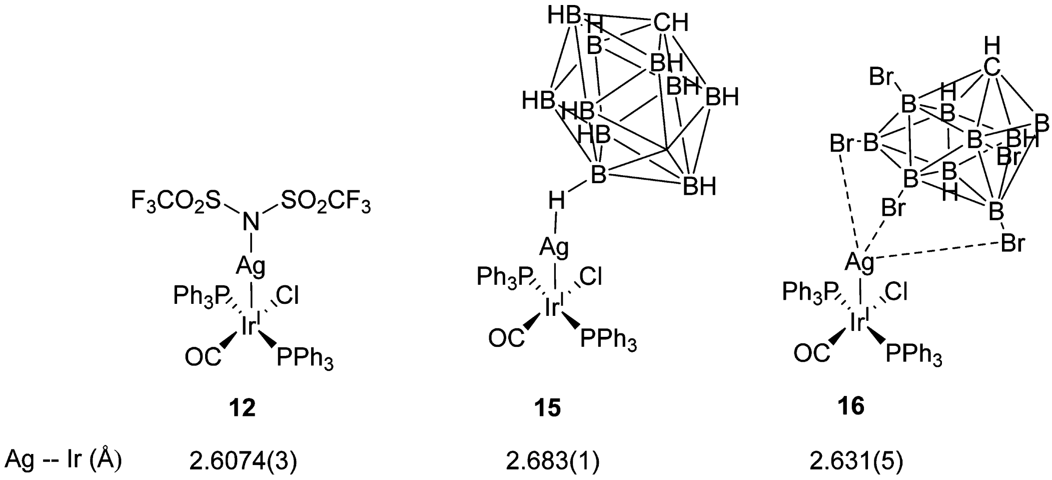
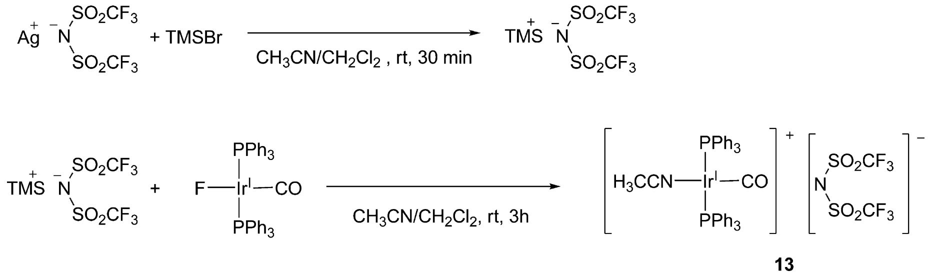


Figure 1. Vaska complex with adducts of silver anions.

Scheme 4. Synthesis of [*trans*-Ir(CH$_3$CN)(CO)(PPh$_3$)$_2$][N(SO$_2$CF$_3$)$_2$] (13)



the triphenylphosphine ligand of *trans*-Ir(Cl)(CO)(PPh$_3$)$_2$. The reaction was complicated by the mostly insoluble silver dinitramide salt.

The complexes are stable to oxygen in the solid state. Complexes **6**−**9** containing the amide or carbamate substituents were also stable to oxygen in solution, while complexes **10** and **11** readily react with oxygen in the air to form the O$_2$ adducts in solution similar to *trans*-Ir(Cl)(CO)(PPh$_3$)$_2$ sensitivity to O$_2$ in solution. The reduced reactivity of complexes **6**−**9** to O$_2$ is unusual for Ir(η^1-nitrogen acid)(CO)(PPh$_3$)$_2$ and may be correlated to the electron-withdrawing nature of the nitro/nitroso conjugate bases. All the new complexes have similar solubility properties as *trans*-Ir(Cl)(CO)(PPh$_3$)$_2$ which are recrystallized from CH$_2$Cl$_2$/CH$_3$OH solvent systems except for **9** which contains the nitroso substituent and is soluble in most solvents except for alkanes.

The reaction of silver bistrisflimide with *trans*-Ir(Cl)(CO)(PPh$_3$)$_2$ did not result in the displacement of the chloride anion by the bistriflimide anion to give AgCl. The unexpected Vaska complex silver bistriflimide adduct **12** was instead isolated along with significant amounts of *trans*-Ir(Cl)(CO)(PPh$_3$)$_2$ (Scheme 3).

Changing the reaction conditions to either benzene or toluene at reflux did not cause the displacement of the chloride ligand by the bistriflimide anion. The silver bistriflimide salt is relatively insoluble in the reaction solvents used but becomes more soluble after reflux. There are two other Ag adducts of Ir(Cl)(CO)(PPh$_3$)$_2$ that have also been characterized with weakly coordinating anions, in these cases with anionic carborane clusters such as **15** and **16** (Figure 1).[17] These clusters are not only weakly coordinating, as is the bistriflimide anion, but they are also bulky. Thus, in these cases both steric and electronic factors may account for the unsuccessful silver metathesis reactions.

There are also other examples of silver adducts with Ir complexes, and in almost all cases[18] the silver salt contains weakly coordinating or electron-withdrawing anions such as trifluoromethanesulfonate (CF$_3$SO$_3^-$), difluorophosphinate (F$_2$PO$_2^-$), and trifluoroacetate (CF$_3$CO$_2^-$).

The poor coordination ability of the bistriflimide anion is even more apparent when an alternative preparation using

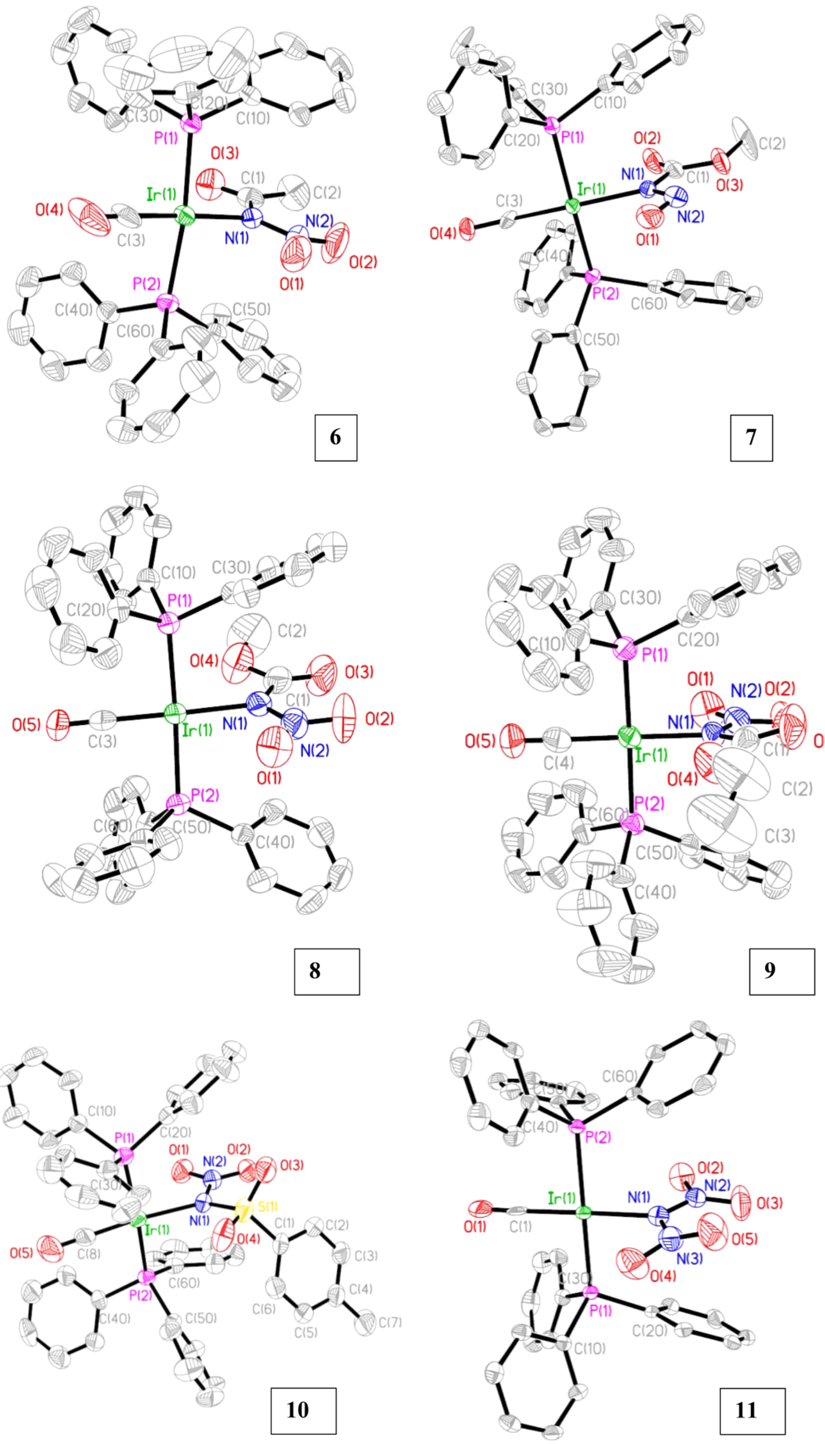


Figure 2. Molecular structures of **6**−**11** with 50% probability thermal ellipsoids. Hydrogen atoms and solvent molecules have been omitted for clarity.

trans-Ir(F)(CO)$(PPh_3)_2$ with [TMS][$N(SO_2CF_3)_2$] (TMS = trimethylsilyl) generated from TMSBr with Ag[$N(SO_2CF_3)_2$] was successful only when CH_3CN is present to give **13** (Scheme 4).

Complex **13** is similar to the [Ir(CH_3CN)(CO)$(PPh_3)_2$]-[ClO_4^-] complex obtained from the metathesis of Vaska's complex and $AgClO_4$ in CH_3CN.[19] This method exploits the strength of Si−F bond formation[20] between the TMS cation and the fluoride ligand on the starting Ir complex. However, the reaction without the presence of CH_3CN gives an amorphous solid that decomposes slowly into a red oil on purification.

Crystallogrpic and Spectroscopic Properties. The molecular structures of **6**−**11** are shown in Figure 2

The Ir complexes in Figure 2 have a trans-square-planar geometry with the triphenylphosphine ligands trans to each other, while the carbonyl (CO) ligand is trans to the respective amides of interest. The conjugate bases of the nitrogen acids are coordinated to the Ir center through the nitrogen of the amide function, and each planar anion has its plane orthogonal

Table 1. ν(CO) Values (cm^{-1}), Bond Lengths (Å), and Bond and Torsion Angles (deg) of Ir(η^1-X)(CO)(PPh_3)$_2$ Complexes, Ir(Cl)(CO)(PPh_3)$_2$·Ag[N(SO_2CF_3)$_2$], and [Ir(CH_3CN)(CO)(PPh_3)$_2$][N(SO_2CF_3)$_2$]

	6	**7**[a]	**8**[b]	**9**[c]	**10**[d]	**11**[e]	**12**[f]	**13**[g]
ν(CO)	1968	1965	1959	1968	1977	1981	2011, 1987	1979
Ir(1)−C(3)	1.804(4)	1.814(6)	1.821(4)	1.803(10)	1.786(6)	1.865(6)	1.857(4)	1.783(10)
Ir(1)−N(1)	2.111(3)	2.131(4)	2.114(3)	2.092(8)	2.146(4)	2.104(5)		2.016(9)
C(3)−O(4)	1.141(5)	1.127(6)	1.125(4)	1.176(10)	1.152(6)	1.060(7)	1.138(5)	1.170(11)
N(1)−N(2)	1.363(4)	1.351(6)	1.367(4)	1.330(12)	1.367(6)	1.343(7)	1.607(3)	
N(1)−C(1)	1.393(5)	1.377(7)	1.384(5)	1.407(13)	1.673(4)	1.449(7)	1.615(3)	
N(2)−O(1)	1.233(5)	1.225(6)	1.220(4)	1.260(11)	1.237(5)	1.200(6)/ 1.247(7)		
N(2)−O(2)	1.221(5)	1.229(6)	1.221(4)		1.222(5)	1.245(6)/ 1.189(6)		
C(3)−Ir(1)−N(1)	175.17(18)	176.6(3)	176.78(15)	179.5(4)	170.7(2)	174.5(2)	78.47(12)	178.8(4)
O(4)−C(3)−Ir(1)	177.3(5)	177.8(7)	178.8(4)	178.8(8)	178.6(6)	177.7(7)	178.0(3)	179.1(9)
O(1)−N(2)−N(1)−C(1)	175.7(4)	−179.6(5)	−169.9(3)	−179.4(8)	−171.2(4)	−172.5(5)		
O(3)−C(1)−N(1)−N(2)	177.1(3)	4.1(9)	12.6(6)	−178.9(9)	48.8(4)	15.8(8)		

[a] O(5) instead of O(4). [b] C(4) instead of C(3) and O(5) instead of O(4). [c] O(2) instead of O(3). [d] C(8) instead of C(3), O(5) instead of O(4), and S(1) instead of C(1). [e] C(1) instead of C(3), O(1) instead of O(4), O(2) and O(4) instead of O(1), O(3) and O(5) instead of O(2), N(3) instead of C(1), and O(5) instead of O(3). [f] C(1) instead of C(3), O(1) instead of O(4), S(1) instead of N(2), and S(2) instead of C(1). [g] N(1) refers to CH_3CN.

to that defined by the iridium square plane. The trans arrangement of the conjugate base of the nitrogen acid to the carbonyl ligand induces a strong electronic effect on the carbonyl ligand mostly through dπ orbital interactions. This effect is most easily observed in the IR stretching frequency of the CO ligand. The reduction in the electron-donating ability of the Ir center (due to competition from the π-accepting ligand trans to the CO) from the off-axis d orbitals into the π^* orbitals of the carbonyl ligand increases the bond order of the CO ligand. This results in the shift of the Ir−CO stretch to higher wavenumbers (closer to the free CO stretch of 2147 cm^{-1}). The CO stretching frequencies, ν(CO), of **6**−**11** are given in Table 1.

In general, there is a shift to higher wavenumbers in ν(CO) on coordination of the new *N*-nitro/*N*-nitroso amide/carbamate/sulfonamide ligands. At first glance this observation supports the hypotheses that the electron-withdrawing nitro and nitroso functional groups on the ligands makes them more π acidic. Also, it is tempting to assess the strength of the π-accepting nature of these ligands from the extent of the shift in the ν(CO) stretch of the starting Vaska complex, which is at 1954 cm^{-1} in a KBr matrix. However, the CO and NR_2 ligands are markedly different π acceptors, with the frontier LUMO of CO having an effective cylindrical symmetry around the Ir−C bond while the NR_2 ligand has a well-defined planar geometry and thus a LUMO symmetrically disposed around the plane. Thus, although there is effective competition for back-bonding by CO and NR_2, this will only affect one of the two off-axis orbitals. In a Cartesian coordinate system with x defined by the N−Ir−C axis and z the vacant coordination sites on the iridium, although d_{xy} can back-bond with both ligands, only CO can back-bond to d_{xz}. Given this expectation, it is perhaps surprising that there is as much variation in ν(CO) for **6**−**11** as there is. Binding of CO is often described as synergistic, with mutual σ and π bonding reinforcing one another, or not. Here the relatively short Ir−N bonds may indicate stronger σ interactions, and this is in keeping with the formal sp^2 hybridization at these nitrogens. This suggests a strong trans influence for this class of donors, but this is difficult to assess from our data.

The reduced π basicity of the nitrogen acids may also play a role in the increase of ν(CO) for the Ir(I) carbonyl nitrogen acid complexes. The presence of electron-withdrawing nitro/nitroso functional groups will also stabilize the filled pπ orbitals of the nitrogen acid ligands, which makes them less available for interaction with the Ir dπ orbitals in comparison to the chloride anion in *trans*-Ir(Cl)(CO)(PPh_3)$_2$. This will result in reduced π basicity of the ligand trans to the carbonyl ligand, which strengthens the carbonyl bond. It is therefore likely that a combination of the increased π-accepting and reduced π-donating properties of the nitrogen acids result in the increased ν(CO) for the Ir(I) carbonyl nitrogen acid complexes.

Complex **11** with dinitramide as the ligand has the highest ν(CO) among the new Ir(I) carbonyl nitrogen acid complexes at 1981 cm^{-1}. This is not surprising, as dintramide contains two nitro groups. The free acid of dintramide is known to be a very strong acid, as the dinitramide anion is a very weak conjugate base from the inductive effect of the nitro groups on the amide nitrogen atom. The *N*-nitrosulfonamide Ir complex **10** has the next highest ν(CO) value at 1977 cm^{-1}. This is followed by *N*-nitrosocarbamate Ir complex **9** and *N*-nitroamide Ir complex **6**, which have similar ν(CO) values and are the next highest after **10** and **11**. Finally, the *N*-nitrocarbamate Ir complexes **7** and **8** have the lowest ν(CO) values in the whole series. The sulfonamide has greater electron-withdrawing properties than the carboxamide, which in turn is stronger than those of the carbamates. The nitroso group has also a greater electron-withdrawing effect than the nitro group from direct comparison between **8** and **9**.

There have been a few studies of analogues of Vaska's complex where the chloride ligand is substituted for various anionic ligands, some of which contain electron-withdrawing groups such as fluoride, nitrite,[2b,21] cyano,[2b] isocyanate,[2b,c,21] trifluoroacetate,[2c] perchlorates,[22] benzotriazole,[23] and even the pseudohalogen nitrosodicyanomethanide.[24] In all of the examples except for X = fluoride, the ν(CO) stretch was higher than that of Vaska complex between 1965 and 1990 cm^{-1}. For X = F the ν(CO) stretch is unexpectedly low at around 1945 (Nujol) or 1957 cm^{-1} ($CHCl_3$). The observed ν(CO) values give a general trend of the π-acidic properties of the ligands, and this can be compared to the Ir−N bond lengths

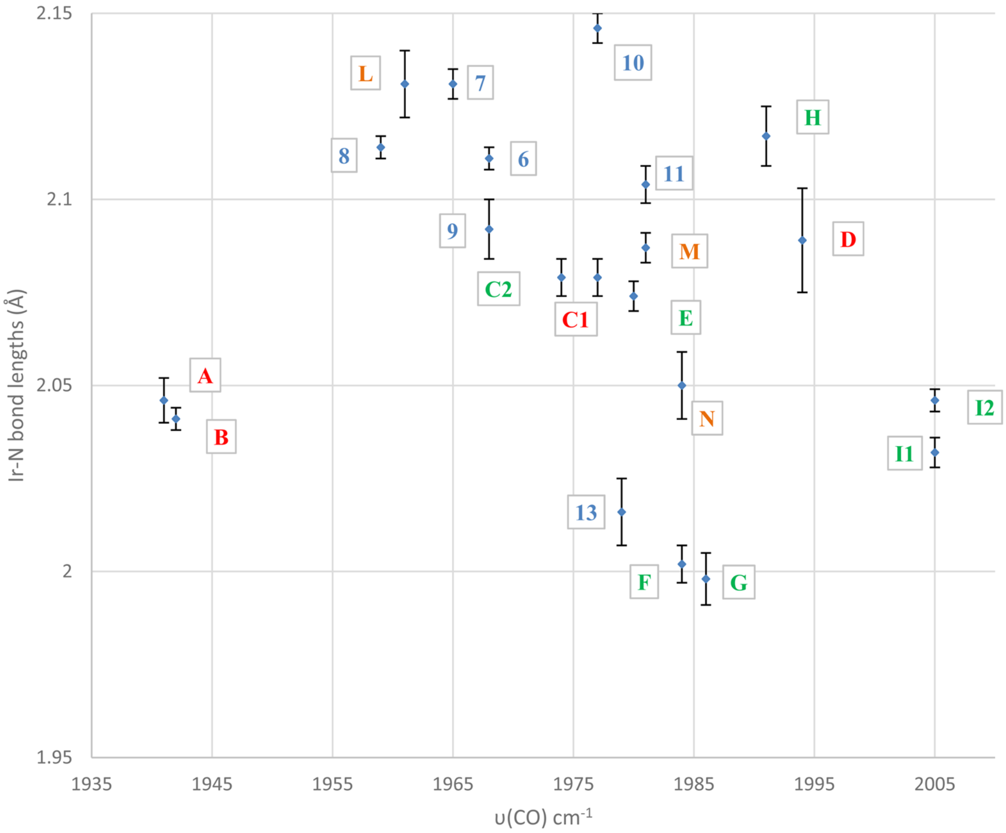


Figure 3. Comparison of Ir−N bond length (Å) versus ν(CO) (cm^{-1}) stretch of Ir^{I}(X)(CO)(PPh$_3$)$_2$, where X is a nitrogen coordination ligand: complexes A, B, C1, and D, solution; complexes C2 and E−I, Nujol; complexes L−N, KBr. X ligands: A, 1,3-dimethylphenylamide; B, *p*-tolylamide; C1, C2, 3,5-bis(trifluoromethyl)pyrazole; D, nitrosodicyanomethanide; E, benzotriazole; F, μ_2-N(Os)bis(3,4-toluenedithiolate); G, μ_2-N(Os)O$_3$; H, 2-(2′-thienyl)pyridine; I, TCM (2,2-dicyanoethylideneamino); L, 8-methylquinolyl; M, tetrafluorosuccinimidato-*N*; N, cyano-Re/Te cluster.

of nitrogen-coordinated Ir(I) carbonyl complexes in the solid state, as shown in Figure 3.

The type of matrix used may have an effect on the observed ν(CO) values, and thus the complexes are grouped according to the reported matrix. The more π-accepting the ligand, the higher the ν(CO) values for the complex. This may also lead to a shorter Ir−N bond due to the increased back-bonding from the metal center. However, from Figure 3 it is seen that no such general trend is observed. The nitrogen acid complexes are generally π acidic, but the Ir−N(1) bonds are summarily longer than those of most of the other nitrogen-based ligands.

As a class Ir(X)(CO)(PR$_3$)$_2$ complexes react with O$_2$ to give Ir^{III}(O$_2$) adducts, where the nature of the anionic and phosphine ligands affect both the rate and reversibility of the oxidative addition of O$_2$. For Vaska's complex itself, X = Cl, R = Ph, the addition is reversible, while for the corresponding iodide, X = I, R = Ph, it is not. Generally it has been found that electron-donating anions increase the rate of the addition while electron-withdrawing anions decrease the rate,[2c,25] especially for cylindrically symmetric anions.[26] This reactivity pattern is also observed for **6**−**9**, where handling solutions of these complexes under aerobic conditions did not result in detectable formations of the Ir^{III}(O$_2$) adducts by ^{31}P NMR and IR spectroscopy or elemental analysis. However, solutions of **10** and **11** are surprisingly reactive, especially **10**, which rapidly takes up O$_2$, as seen by its rapid change in solution color from yellow to orange and a new ν(CO) band in the IR at 2030 cm^{-1} ν(CO) and a new ^{31}P resonance signal at 3.28 ppm. This is very surprising, as these complexes have the two highest ν(CO) values in the series. There may be some evidence of a geometry-induced reactivity from the anionic ligand. Complexes **10** and **11** are shown to have the largest nonlinear C(carbonyl)−Ir−N(1) angles of 170.7(2) and 174.5(2)°, respectively (Table 1). The increasingly bent C(carbonyl)−Ir−N(1) angle changes the geometry of the Ir complex toward trigonal bypyrimidal and is likely to increase the d$_{z^2}$ orbital or HOMO energy level, resulting in an increase in the reaction coordinate toward oxidative addition of O$_2$.

The bond lengths (Table 1) of the nitrogen acid conjugate bases in the Ir(I) complexes follow the general trend of the potassium salt of the nitrogen acids.[16] The N(1)−N(2) bond lengths are shorter and the N(1)−C(1)/S(1) bond lengths are longer in the new Ir(I) complexes in comparison to those in the free acid forms. The N(2)−O(1)/O(2) bond lengths are also longer in the Ir(I) complexes in comparison to those in the free acid, which in turn are similar to those in the potassium salts. The O(1)−N(2)−N(1)−C(1) torsion angles for the nitrogen acid ligands have increased deviation from planarity, which implies reduced conjugation between the "NNO$_2$/NNO" fragment and the acyl fragment of the ligand. This structural change is also observed in the potassium salts. An increase in the alkyl chain on the acyl fragment is also observed to lead to an increase in the nonplanarity. The *N*-nitrosocarbamate ligand in **9** is also different from the *N*-nitro nitrogen acid ligand complexes. The N(1)−N(2) bond of **9** is significantly shorter and the N(1)−C(1) longer than those in the other N-nitro nitrogen acid complexes (Table 1). There is also a pronounced elongation of the nitrosyl N−O bond lengths in comparison to

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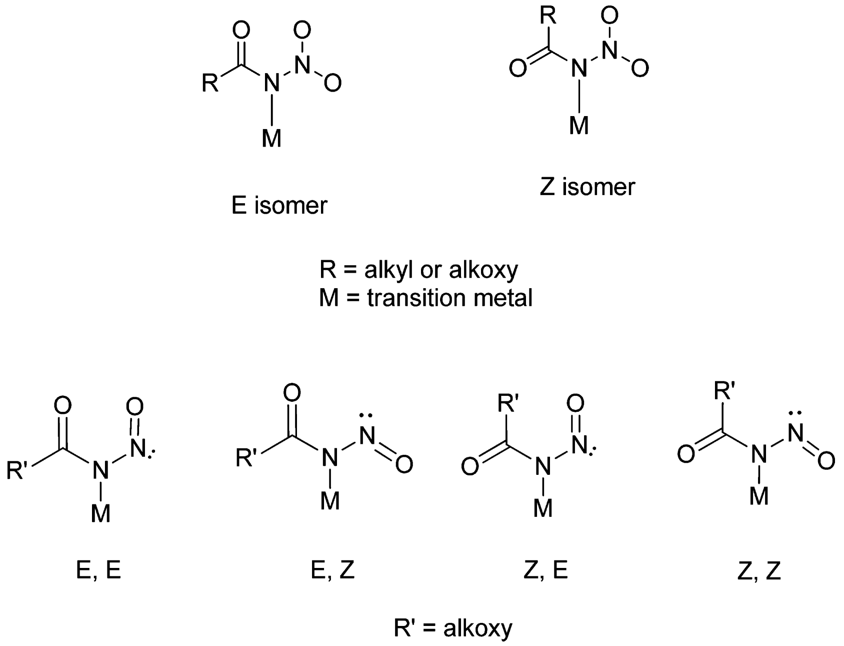

Figure 4. Possible configuration isomers for Ir(I) nitrogen acid complexes.

the nitro N−O bond lengths. These structural differences may indicate the *N*-nitroso ligand to be prime toward decomposition with the release of N_2.

In addition to these changes in metric parameters upon coordination, there are general conformation trends of the nitrogen acid ligand upon coordination to the Ir center. There are two possible conformations for the *N*-nitroamides/*N*-nitrocarbamates, *E* or *Z*, and four for the *N*-nitrosocarbamates (*E*,*E*, *E*,*Z*, *Z*,*E*, and *Z*,*Z*). On the basis of conventions, the *E*/*Z* isomerism for ligands coordinated to transition-metal complexes may be different from that of the free acid or the conjugate base anions (Figure 4).

For **7** and **8**, the nitrogen acid ligand has the *E* configuration, which is similar to that for both the free acid and the conjugate base potassium salt. For **6**, the *N*-nitroacetamide ligand is observed to adopt the *Z* configuration, which differs from that of both the free acid and the potassium salt. Finally for **9**, the *N*-nitrosomethylcarbamate ligand is observed to take up the *Z*,*Z* configuration while the free acid and conjugate base potassium salt have the *Z*,*E* configuration. These configurations reflect the energy barriers that result from the delocalized π bonding in these anions.

The solid-state structure of **11** is observed to share the unusual bond parameters of the dinitramide ligand, which have been reported before for other dinitramide metal complexes.[8,9c] The first unusual feature is that the two NO_2 groups are nonplanar to each other with a deviation of approximately 15.8°. The second unusual feature is that there are inequivalent N−O bond lengths within the same nitro group.

The reaction of Vaska's complex with $Ag[N(SO_2CF_3)_2]$ gave the unusual bimetallic silver adduct **12**, the molecular structure of which is shown in Figure 5.

The geometry around the Ir center is that of a square pyramid with the triphenylphosphines, chloride, and carbonyl ligands forming the square base and Ag(1) poised 2.660 Å above the P−Cl−C−P plane. The Ag(1)−Ir(1) bond length indicates some Ir−Ag interaction and is similar to those of other Ag−Ir adducts shown in Figure 1. The position of the silver cation is along the *z* axis of the original Vaska complex, likely due to interaction with the d_{z^2} HOMO orbital. The Ag(1)−N(1) interaction in **12** is significantly shorter than those of other silver bistriflimide adduct salts, which have been reported to be between 2.344(6) and 2.515(4) Å.[27]

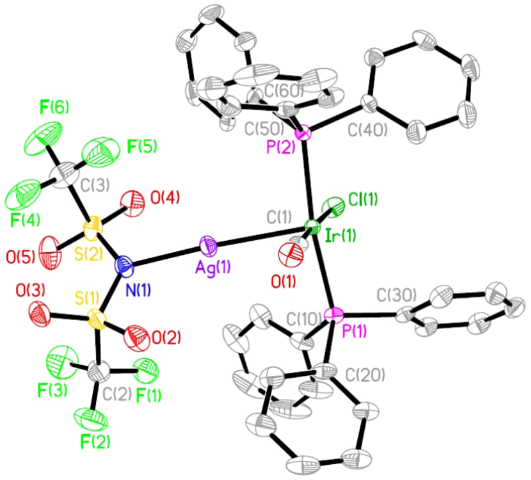

Figure 5. Molecular structure of **12** with 50% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected metrical values: Ag(1)−Ir(1) = 2.6074(3) Å, Ag(1)−N(1) = 2.160(3) Å.

Complex **13** contains a square-planar cationic Ir(I) center with the bistriflimide anion not coordinated to the Ir atom (Figure 6). The ligand situated trans to the carbonyl ligand is an acetonitrile ligand that was used as a solvent in one of the reaction steps. The Ir−N bond length is similar to those of the other complexes, but the ν(CO) stretch of 1979 cm^{-1} is higher than the ν(CO) values of the Ir nitrogen acid carbonyl complexes. The severe disorder associated with the bistriflimide anion in **13** limits any meaningful comparison with the bistriflimide anion in **12**.

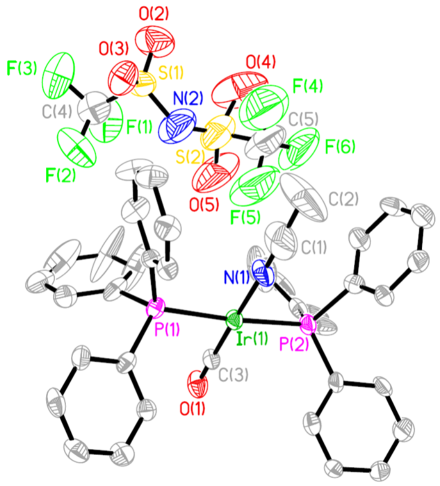

Figure 6. Molecular structure of **13** with 50% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity. The bistriflimide anion is disordered.

CONCLUSION

The facile synthesis of the nitrogen acid derivatives of Vaska's complex, *trans*-Ir(nitrogen acid)(CO)$(PPh_3)_2$ (**6**−**10**), suggests that these anions are suitable ligands for a variety of transition-metal complexes. Depending on the reaction methodology, these nitrogen acids are able to form either singly bound (above) or doubly coordinated ligands (Ir^{III} system),[4a] depending on the coordination sphere of the metal center. The ν(CO) values of these complexes indicate that these anions behave mostly as π acceptors. The dinitramide and bistriflimide anions are much stronger π acids, which are shown in the much higher ν(CO) values and also the lower nucleophilicity for substitution of the chloride anion in Vaska's complex. Silver bistriflimide is found to form a Ir−Ag adduct complex. A new synthetic methodology to form Ir(I) carbonyl complexes for poorly coordinating ligands has been shown to be successful using *trans*-Ir(F)(CO)$(PPh_3)_2$ with silver salts in the presence of trimethylsilyl halide. The first example of an *N*-nitrosocarbamate/amide transition-metal complex, **9**, has been fully characterized. The *N*-nitroso group is observed to have slightly more π acidic properies in comparison to those of the *N*-nitro analogue from the higher ν(CO) values. Further investigation into the reactivity of these new complexes with acids, and other oxidative addition reactions will be made.

ASSOCIATED CONTENT

Supporting Information

Text, a table, a figure, and CIF files giving details of the synthesis of *N*-nitrosomethylcarbamate, X-ray diffraction data for **6**−**13**, information on the crystallographic parameters of the determined structures (Table S1), and reference information for complexes **A**−**P**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for **6** (965827), **7** (965605), **8** (965604), **9** (965606), **10** (965607), **11** (965603), **12** (965602), and **13** (1036371) are also available at the CCDC, with the CCDC file numbers in parentheses.

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Notes

The authors declare no competing financial interest.

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