COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Synthesis, structure, and reactions of a nitroxyl complex of iridium(III), *cis*,*trans*-$IrHCl_2(NH{=}O)(PPh_3)_2$

Rory Melenkivitz and Gregory L. Hillhouse*

Searle Chemistry Laboratory, Department of Chemistry, The University of Chicago, Chicago, Illinois 60637, USA. E-mail: g-hillhouse@uchicago.edu

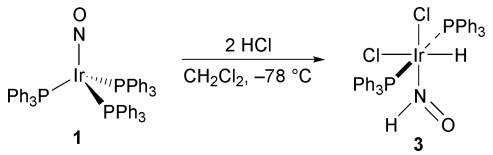
Received (in Purdue, IN, USA) 21st December 2001, Accepted 6th February 2002
First published as an Advance Article on the web 27th February 2002

Reaction of $Ir(NO)(PPh_3)_3$ with anhydrous HCl results in addition of 2 equivalents of HCl with formal protonation of the nitrosyl ligand, affording the unusual six-co-ordinate nitroxyl complex *cis*,*trans*-$IrHCl_2(NH{=}O)(PPh_3)_2$.

Nitroxyl (HN=O) is a highly reactive, unstable molecule attracting current interest primarily because of its relationship to nitric oxide. The nitrosonium cation (NO^+) and the nitroside anion (NO^-), as well as the conjugate acid of NO^-, nitroxyl, have been suggested to be responsible for some of the myriad functions attributed to nitric oxide in mammalian biochemistry.[1] Interest in HN=O also stems from its postulated intermediacy in photochemical and free-radical reactions and the role its formation and decomposition may play in mechanisms for the combustion of nitrogen-containing fuels and the oxidation of atmospheric nitrogen.[2] In some of these functions, metal co-ordination is likely involved, for example in HN=O co-ordination to heme iron,[3] so knowledge of how nitroxyl interacts with and is stabilised by metals is desirable. We and others have been interested in elucidating the co-ordination chemistry of this novel molecule.[3–7] Two nitroxyl complexes have been structurally characterised, $OsCl_2(NH{=}O)(CO)(PPh_3)_2$ by Roper and Ibers,[5] and $Ru(NH{=}O)$\{2,6-bis(2-mercapto-3,5-di-*tert*-butylphenylthio)dimethylpyridine\} by Sellmann.[6]

Roper and co-workers have previously observed that reaction of the four-co-ordinate nitrosyl complex $Ir(NO)(PPh_3)_3$ (**1**) with an excess of HCl results in reduction of the nitrosyl ligand of **1** to give a six-co-ordinate iridium(III) hydroxylamine derivative, $IrCl_3(NH_2OH)(PPh_3)_2$ (**2**).[5a,8] We were interested in reinvestigating this reaction in an attempt to intercept the intermediates in what clearly is a multi-step reaction. Possible intermediates, such as $IrCl(NH{=}O)(PPh_3)_2$ (a *Vaska's complex* analogue), seemed reasonable since, like carbon monoxide, ligated nitroxyl is a strong π-acid.[4b] A comparison of ν_{CO} in $Re(NH{=}O)(CO)_3(PPh_3)_2^+$ (2082, 2007, 1977 cm^{-1}) with ν_{CO} in $Re(NH_2OH)(CO)_3(PPh_3)_2^+$ (2061, 1966, 1926 cm^{-1}) shows a large increase in ν_{CO} ($\Delta \sim 21$–51 cm^{-1}) when the purely σ-donating NH_2OH ligand is replaced by the HN=O ligand in an otherwise identical co-ordination environment. This reflects substantial competition for metal π-electron density by a π* orbital of the nitroxyl ligand (backbonding), and this has been further supported by DFT calculations.[4b]

Reaction of **1**[8] with a controlled excess of anhydrous HCl (CH_2Cl_2, −78 °C) gives *cis*,*trans*-$IrHCl_2(NH{=}O)(PPh_3)_2$ (**3**) as pink crystals in 60% isolated yield (eqn. 1).† The labelled isotopomer *cis*,*trans*-$IrHCl_2(^{15}NH{=}O)(PPh_3)_2$ (**3-^{15}N**) was analogously prepared from $Ir(^{15}NO)(PPh_3)_3$. Use of three equivalents of HCl seems to afford optimal yields of **3**, whereas addition of a single-equivalent of acid results in reduced yields of **3** and recovered starting material. Complex **3** was characterised by NMR (^1H and ^{31}P) and infrared spectroscopy, elemental analysis, and a single crystal X-ray diffraction study.‡ The infrared spectrum of **3** shows vibrations associated with the nitroxyl ligand (ν_{NO} = 1493(s), ν_{NH} = 2810(w) cm^{-1}) which are isotopically shifted in the infrared spectrum of **3-^{15}N** (ν_{NO} = 1465(s), ν_{NH} = 2801(w) cm^{-1}).



(1)

The ^1H NMR spectrum of **3** exhibits the diagnostic downfield resonance expected for the nitroxyl ligand's proton (δ 22.75)[3–6] and a characteristic upfield resonance for the hydride ligand (δ −18.90, triplet, $^2J_{PH}$ = 27.8 Hz). In the ^1H NMR spectrum of **3-^{15}N**, the nitroxyl proton resonance appears as a doublet-of-triplets in which both the ^{15}N–H (77.6 Hz) and ^{31}P–H (1.7 Hz) couplings are resolved. The value of $^1J_{NH}$ is in the range expected for a proton attached to an sp^2-hybridized nitrogen co-ordinated to a transition metal, and is similar to those reported for other nitroxyl and related diazene complexes.[3,4,5b,9]

The molecular structure of **3** is shown in Fig. 1, and Table 1 summarises pertinent bond lengths and angles for **3** and the other structurally characterised nitroxyl complexes. The d^6 iridium adopts a pseudo-octahedral co-ordination geometry with *trans* phosphines and *cis* chlorides. The hydride ligand was not crystallographically located, but it exerts a typical *trans*-lengthening influence on Cl(2) relative to Cl(1). The nitroxyl ligand lies in the molecule's (non-crystallographic) mirror plane, which allows for backbonding with an orthogonal filled d-orbital of π-symmetry. Although there is no evidence for

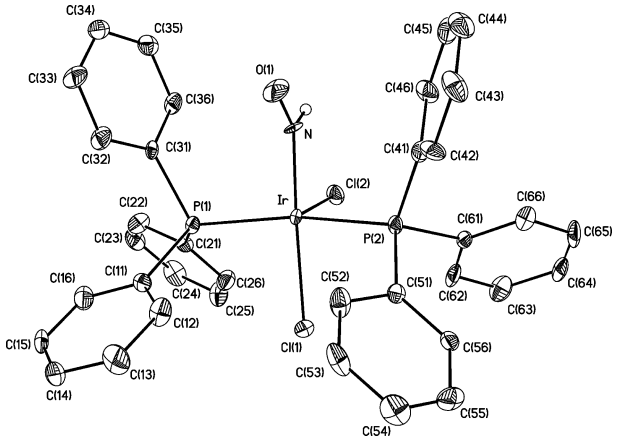


Fig. 1 A view of the molecular structure of **3**. Selected metrical parameters: Ir–N = 1.879(7), N–O(1) = 1.235(11), Ir–Cl(1) = 2.403(2), Ir–Cl(2) = 2.476(2), Ir–P(1) = 2.351(3), Ir–P(2) = 2.345(3) Å; Ir–N–O(1) = 129.8(7), N–Ir–Cl(2) = 83.6(3), N–Ir–Cl(1) = 177.0(3), N–Ir–P(1) = 94.2(3), N–Ir–P(2) = 93.0(3), P(1)–Ir–P(2) = 165.19(8)°.

Table 1 Comparison of bond lengths and angles for HN=O ligands

Compound	M–N/Å	N–O/Å	M–N–O/°
$IrHCl_2(NH{=}O)(PPh_3)_2$ (**3**)[a]	1.879(7)	1.235(11)	129.8(7)
$OsCl_2(NH{=}O)(CO)(PPh_3)_2$[b]	1.915(6)	1.193(7)	136.9(6)
$Ru(S_4py)(NH{=}O)$[c]	1.875(7)	1.242(9)	130.0(6)

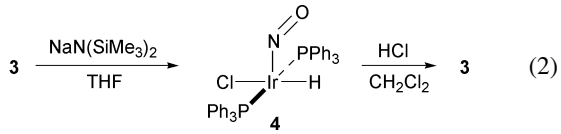
[a] This work. [b] Ref. 5*b*. [c] Ref. 6.

DOI: 10.1039/b111645b

intramolecular hydrogen bonding, the nitroxyl proton is oriented *syn* to Cl(2), a structural feature common to both **3** and $OsCl_2(NH{=}O)(CO)(PPh_3)_2$.[5b] The spectroscopic and structural data clearly show that the nitrosyl ligand has undergone protonation at nitrogen, but it is noteworthy that O-protonation of the nitrosyl ligand of $(C_5Me_5)W(NO)(R)_2$ (R = CH_2Ph, CH_2SiMe_3) to give hydroxylimido complexes has recently been reported.[10]

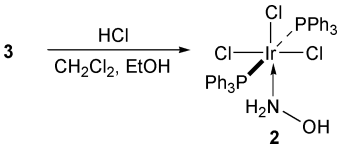
Reaction of **3** with $NaN(SiMe_3)_2$ in THF solution results in its dehydrohalogenation to give the five-co-ordinate nitrosyl hydride complex $IrHCl(NO)(PPh_3)_2$ (**4**, eqn. 2). The Ir–H resonance for **4** appears at δ −18.65 (triplet, $^2J_{PH}$ = 30.6 Hz) in the ^{1}H NMR spectrum, and equivalent phosphine ligands are indicated by a singlet resonance at δ 18.85 in the $^{31}P\{^1H\}$ spectrum. The infrared spectrum shows a strong band for ν_{NO} at 1548 cm^{-1} (which compares well with the literature value of 1545 cm^{-1} for **4** prepared by an independent route).[8] The spectroscopic similarity between **4** and the crystallographically characterised complex $IrCl_2(NO)(PPh_3)_2$ (ν_{NO} = 1560 cm^{-1}; δ Ir–PPh_3 = 11.6)[11] gives further support to the square-pyramidal structure of **4** shown in eqn. 2. Related conversions of nitroxyl ligands to nitrosyls by base have been described.[4b,5a]

In a key experiment, treatment of CH_2Cl_2 solutions of isolated samples of **4** with anhydrous HCl cleanly gives **3** (eqn. 2). This indicates that the mechanism for formation of **3** from **1** likely involves initial oxidative addition of HCl to form **4**. The subsequent reaction of **4** with the second equivalent of acid to give **3** must be fast relative to the first step since no intermediate is observed in the transformation of **1** to **3**.



(2)

Finally, a comment on the relevance of **3** as an intermediate in the reduction of the nitrosyl ligand of **1** to the hydroxylamine ligand of $IrCl_3(NH_2OH)(PPh_3)_2$ (**2**) is in order. Interestingly, addition of anhydrous HCl to a pure sample of **3** in methylene chloride does not result in further reduction of the nitroxyl ligand. (In fact, in our synthesis of **3**, addition of a slight excess of acid gives the best yields, *vide supra*.) However, addition of EtOH to solutions of **3** containing HCl results in the rapid conversion of **3** to the hydroxylamine derivative **2** (eqn. 3).§ The exact role of EtOH in this reaction is unclear, but it probably involves acid solvation. Reduction of the nitroxyl ligand is formally effected by the delivery of H^- (from the Ir–H) and H^+ (from the acid). In Roper's original reports of the preparation of $IrCl_3(NH_2OH)(PPh_3)_2$, aqueous HCl was used to carry out protonation of **1** (alternatively, anhydrous HCl was used along with ethanol as a co-solvent),[5a,8] and it was the aqueous conditions and ethanolic workup that prevented the isolation of the iridium nitroxyl intermediate.



(3)

This research was supported by grants from the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society (to G. L. H.), and by a GAANN Fellowship from the U. S. Department of Education (to R. M.). We thank Dr. Daniel Mindiola for crystallographic assistance.

Notes and references

† To a sample of **1** (0.36 g, 0.47 mmol) dissolved in 8 mL of CH_2Cl_2 and cooled to −78 °C was added 3 equiv. of anhydrous HCl *via* a calibrated volume. The red solution was stirred for 20 min, the volume was reduced to 3 mL, and a toluene/pentane mixture was added to induce crystallisation. The resulting pink powder was purified by recrystallisation from dichloromethane/pentane, yielding pure **3** (0.24 g, 0.28 mmol, 60%). For **3**: ^{1}H NMR (CD_2Cl_2, 298 K) δ 22.75 (s, 1 H, Ir–N*H*=O), 7.1–7.3 (m, 30 H, Ph), −18.90 (t, 1 H, Ir–*H*, $^2J_{PH}$ = 27.8 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K) δ −1.73 (s). IR (CaF_2/fluorolube mull): 2810 (w, ν_{NH}), 1493 (s, ν_{NO} cm^{-1}). Anal. Calcd. for $C_{36}H_{32}NCl_2IrOP_2$: C, 52.75; H, 3.93; N, 1.71. Found: C, 52.53; H, 3.80; N, 1.80%.

‡ *Crystal data*: For **3**·4(C_4H_8O), $C_{51}H_{55}Cl_2IrNO_4P_2$, M = 1071.00, triclinic, $P\bar{1}$, a = 9.751(11), b = 11.1216(12), c = 23.281(3) Å, α = 82.508(2), β = 84.582(2), γ = 64.976(2)°, Z = 2, V = 2318.2(4) Å^3, T = 100 K, μ(Mo-Kα) = 3.110 mm^{-1}. Of 13810 total reflections (red needle, 1.77 = θ = 28.33°), 9458 were independent and 7746 (R_{int} = 7.21%) were observed with $I > 2\sigma(I)$. A semi-empirical absorption correction was performed using psi-scans. Patterson methods were used to locate the heavy atoms Ir, Cl, P, and other heteroatoms. No anomalous bond lengths or thermal parameters were noted except for one disordered tetrahydrofuran molecule of solvation which resided at an inversion centre. Three of its carbon atoms (C20s, C21s, C22s) were located and refined, but the complete THF molecule could not be resolved. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically and fit to idealised positions. $R(F)$ = 7.33% and $R(wF)$ = 16.35%. CCDC reference number 178606. See http://www.rsc.org/suppdata/cc/b1/b111645b/ for crystallographic data in CIF or other electronic format.

§ Characterisation of **2** followed by comparison with an authentic sample made by the literature route.[8] For **2**: ^{1}H NMR (CD_2Cl_2, 298 K) δ 8.00 (s, 1 H, OH), 7.7–7.2 (m, 30 H, Ph), 5.38 (s, 2 H, NH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K) δ −30.44 (s).

1 (*a*) A. R. Butler, F. W. Flitney and D. L. H. Williams, *Trends Pharmacol. Sci*., 1995, **16**, 18; (*b*) J. S. Stamler, D. J. Singel and J. Loscalzo, *Science*, 1992, **258**, 1898; (*c*) C. Herce-Pagliai, S. Kotecha and D. E. G. Shuker, *Nitric Oxide*, 1998, **2**, 324; (*d*) K.-D. Kröneke, K. Fehsel and V. Kolb-Bachofen, *Nitric Oxide*, 1997, **1**, 107.
2 (*a*) R. Guadagnin, G. C. Schatz and S. P. Walch, *J. Phys. Chem*., 1995, **102**, 774; (*b*) F. W. Dalby, *Can. J. Phys*., 1958, **36**, 1336.
3 R. Lin and P. J. Farmer, *J. Am. Chem. Soc*., 2000, **122**, 2393.
4 (*a*) J. S. Southern, G. L. Hillhouse and A. L. Rheingold, *J. Am. Chem. Soc*., 1997, **119**, 12406; (*b*) J. S. Southern, M. T. Green, G. L. Hillhouse, I. A. Guzei and A. L. Rheingold, *Inorg. Chem*., 2001, **40**, 6039.
5 (*a*) K. R. Grundy, C. A. Reed and W. R. Roper, *Chem. Commun*., 1970, 1501; (*b*) R. D. Wilson and J. A. Ibers, *Inorg. Chem*., 1979, **18**, 336.
6 D. Sellmann, T. Gottschalk-Gaudig, D. Haussinger, F. W. Heinemann and B. A. Hess, *Chem. Eur. J*., 2001, **7**, 2099.
7 G. LaMonica, M. Freni and S. Cenini, *J. Organomet. Chem*., 1974, **71**, 57.
8 C. A. Reed and W. R. Roper, *J. Chem. Soc. A*, 1970, 3054.
9 (*a*) M. R. Smith III, T.-Y. Cheng and G. L. Hillhouse, *J. Am. Chem. Soc*., 1993, **115**, 8638; (*b*) K. R. Laing, S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Dalton Trans*., 1973, 2713; (*c*) B. L. Haymore and J. A. Ibers, *J. Am. Chem. Soc*., 1975, **97**, 5369; (*d*) C. F. Barrientos-Penna, F. W. B. Einstein, T. Jones and D. Sutton, *Inorg. Chem*., 1983, **22**, 2614; (*e*) G. Albertin, S. Antoniutti, M. Lanfranchi, G. Pelizzi and E. Bordignon, *Inorg. Chem*., 1986, **25**, 950.
10 W. B. Sharp, P. Legzdins and B. O. Patrick, *J. Am. Chem. Soc*., 2001, **123**, 8143.
11 J. A. Ibers and D. M. P. Mingos, *Inorg. Chem*., 1971, **10**, 1035.