Inorganic Chemistry

ARTICLE

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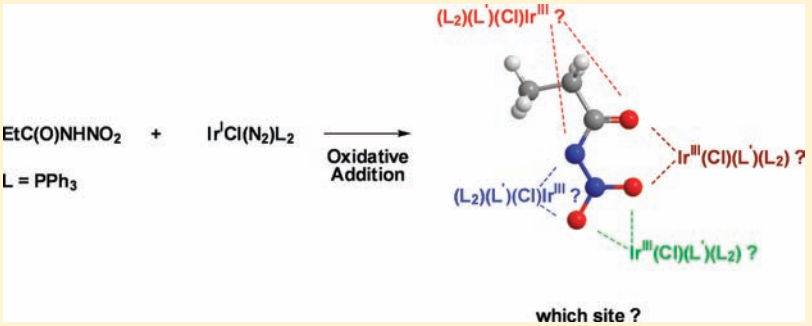
N−H Activation in N-Nitropropionamide: Coordination Chemistry of a Primary Nitroamide

D. Scott Bohle* and Zhijie Chua

Department of Chemistry, McGill University, 801 Sherbrooke St. W. Montreal, H3A 2K6, Canada

Supporting Information

ABSTRACT:



N-nitropropionamide, $EtC(O)NHNO_2$, oxidatively adds to $Ir(Cl)(N_2)(PPh_3)_2$ to give a η^2-(N,O)-N-nitropropionamide anion bound to an Ir hydride complex. Single-crystal X-ray diffraction of the product indicates that it forms an unusual O-bound chelate through the nitro group. Density functional calculations for a model nickel complex, $[Ni(MeC(O)NNO_2)(CN)_2]^-$, are used to help distinguish the observed IR bands for the four possible conformations and binding geometries of this ligand.

INTRODUCTION

Although secondary nitramines, R_2NNO_2, are important industrial compounds with a range of high energy density material applications[1−3] and possible biological roles,[4] the primary nitramines, $RHNNO_2$, are less well-defined. In part, this is due to their sharing similar decomposition pathways to that of nitramide itself.[3,5] Within the primary nitramines, the acyl-substituted derivatives such as N-nitropropionamide, $EtC(O)NHNO_2$, are among the most stable; however, the chemistry of such primary N-nitroamides is sparsely reported. This is due to their difficult, inconsistent, and low yielding preparations by either the acylation of nitramide or the addition of NO_2BF_4 to amides. In this paper, we report on the successful synthesis of N-nitropropionamide and its oxidative addition to an Ir(I) complex to give the first complex of a nitroamide.

EXPERIMENTAL SECTION

Schlenk and inert atmosphere glovebox techniques under a nitrogen atmosphere were employed in the synthesis and handling of air-sensitive compounds. Distilled water and solvents were degassed prior to use when required. The oleum used in the preparation of materials contains 20% free SO_3, and the concentrated HNO_3 used must have a minimum gravimetric density of 1.5 g ml^{-1}. ^1H and ^{31}P NMR spectra were measured on a 200 MHz Varian Mercury FT NMR spectrometer. ESI mass spectra were obtained on Finnigan LCQ_{DUO} spectrometer. Elemental analyses were performed by the Elemental Analysis Laboratory at the University of Montreal. Melting points were obtained from Thermal Analysis Instruments Differential Scanning Calorimeter 2010. Nitramide was prepared using modified procedures described below.

Nitramide. The method of Shreeve et al. for the synthesis of nitramide[6−8] was modified as follows. Oleum(fuming sulphuric acid) (20 g) is added to nitric acid (20 g) in an ice bath ($T < 5$ °C). Urea (5.72 g, 95.3 mmol) is then added in portions between −5 and 0 °C. The reaction mixture is allowed to stir for 40 min between 0 and 5 °C, during which time a white precipitate forms. Some foaming may be observed. The reaction mixture is cooled to −15 °C and filtered, washed with cold trifluoroacetic acid, (TFA; 2 × 15 mL), and squeezed. The white precipitate obtained is dinitrourea. The dinitrourea (14.3 g, 95.3 mmol) is then dissolved in a urea solution (5.75 g, 95.8 mmol in 10 mL of H_2O) at $T < 20$ °C. The mixture is stirred for 15 min and cooled to 5 °C. The dinitrourea−urea salt is collected by filtration, washed with a minimal amount of cold H_2O, and dried in the air. Dinitrourea−urea salt (20.02 g, 95.3 mmol) is added in portions to H_2SO_4 (20.02 g in 50 mL H_2O) at $T < 20$ °C. The reaction is stirred until it is homogeneous and subjected to ether extractions (3 × 80 mL). The wet ether extracts are combined and allowed to hydrolyze for 4 h at room temperature. The ether is removed by rotary evaporation to give a white solid, which is further purified by vacuum sublimation at ∼1 Torr (dry ice−acetone condensor) to give nitramide (3.339 g, 53.9 mmol, 28.3% yield). ^1H NMR ($CDCl_3$, 200 MHz): δ 8.06 (broad, N*H*). IR (KBr, cm^{-1}): 3364 m, 3261 m, 3200 m, 3170 m, 3047s, 1583w, 1567w, 1535s, 1516s, 1414s, 1403s,

Received: January 14, 2011
Published: March 10, 2011

Table 1. Crystallographic Data and Data Collection Parameters for 1 and 2

	1	2
empirical formula	$C_3H_6N_2O_3$	$IrP_2Cl_3O_3N_2C_{40}H_{37}$
temp, K	100(2)	298(2)
cryst sys	monoclinic	triclinic
space group	$P2(1)/m$	$P\bar{1}$
a, Å	4.897(2)	11.2223(17)
b, Å	5.952(3)	12.3960(18)
c, Å	8.852(4)	15.945(2)
α, deg	90	69.818(2)
β, deg	100.975(5)	76.2442(2)
γ, deg	90	74.736(2)
V, Å^3	253.3(2)	1983.1(5)
Z	2	2
density, g cm^{-3}	1.549	1.598
abs coeff, mm^{-1}	0.138	3.689
no. of reflns collected	2199	17642
no. of indep reflns	636	8754
no. of data/restraints/params	636/0/49	8754/0/460
final R indices [$I > 2\sigma(I)$]	R1 = 0.0306; wR2 = 0.0827	R1 = 0.0327; wR2 = 0.0823
R indices (all data)	R1 = 0.0331; wR2 = 0.0851	R1 = 0.0400; wR2 = 0.0878
goodness-of-fit on F^2	1.092	1.047
CDC number	807691	807692

1205 m, 1189 m, 1049w, 783w, 708w, 590w. Raman (solid, cm^{-1}): 1051s, 711w, 576w. UV (EtOH): λ_{max} = 206 nm, ε = 7675 L mol^{-1}cm^{-1}.

Synthesis of N-Nitropropionamide, 1. Nitramide (500 mg, 8.06 mmol) is dissolved in ether (5 mL). The ether solution is cooled to 0 °C in an ice-bath, and propionic anhydride (11 mL, 85.4 mmol) is added. LiCl (0.4 mg, 9.41 μmol) is added, and the reaction mixture is allowed to warm to room temperature and is stirred for 24 h. The product is purified by column chromatography on silica initially using dichloromethane to remove propionic acid and propionic anhydride followed by ethyl acetate/MeOH (3:1) as an eluant, to give a white solid which is further purified by vacuum sublimation (dry ice−acetone) to give N-nitropropionamide (172 mg, 1.46 mmol; 18.1% yield). MP: 83.5 °C. ΔH_{fusion} = +16.9 kJ mol^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.23 (t, 3H, J = 7.3 Hz), 2.77 (q, 2H, J = 7.3 Hz), 10.35 (br, N*H*). IR (KBr, cm^{-1}): 3443w, 3238s, 3206s, 2994w, 2983 m, 2948w, 1729s, 1610s, 1469 m, 1436s, 1412s, 1326s, 1140s, 1070s, 1025 m, 976 m, 802 m, 770w, 745 m, 648 m, 537 m. Raman (solid, cm^{-1}): 2952w, 2932w, 1727 m, 1437w, 1435 m, 1406 m, 1317 m, 1301 m, 1116 m, 1055w, 1027w, 974s, 745 m, 445 m, 364s, 317w.

Synthesis of *trans*-Ir(η^2-$C_2H_5C(O)NNO_2$)(H)(Cl)(PPh_3)$_2$, 2. *trans*-Ir(Cl)(N_2)(PPh_3)$_2$ (156 mg, 0.200 mmol)[9,10] and N-nitropropionamide (28.0 mg, 0.237 mmol) are dissolved in $CHCl_3$ (5 mL) under a N_2 atmosphere. Bubbling is observed, and the reaction mixture is stirred for 3 h. The reaction mixture is evacuated to give a yellow solid. The yellow solid is recrystallized from CH_2Cl_2/CH_3OH to give *trans*-Ir(η^2-$C_2H_5C(O)NNO_2$)(H)(Cl)(PPh_3)$_2$ as yellow crystals (110 mg, 0.126 mmol; 63.2%). MP: 131.4 °C. ΔH_{dec} = −141.4 kJ mol^{-1}. ^{31}P{^{1}H} NMR ($CDCl_3$, 80 MHz): δ 11.56. ^{1}H NMR ($CDCl_3$, 200 MHz): δ −31.65 (br, M-*H*), 0.49 (t, 3H, J, = 7 Hz), 1.44 (q, 2H, J, = 7 Hz), 7.33−7.39 (m, 18H), 7.60−7.70 (m, 12H). IR (KBr, cm^{-1}): 3056 m, 2983w, 2937w, 2311w, 1720 m, 1692 m, 1509s, 1482 m, 1435s, 1222 m, 1168s, 1096s, 1061 m, 999 m, 753 m, 744 m, 706s, 695s, 618w, 522s, 503 m. Raman (solid, cm^{-1}): 3063w, 2314w, 1591 m, 1191w, 1164w, 1099 m, 1031 m, 1002s, 855w, 706 m, 618 m, 543w, 318w. ESI$^+$-MS: m/z 893 [M + Na]$^+$. Anal. Calcd for $IrClP_2O_3N_2C_{39}H_{36}\cdot CH_2Cl_2$: C, 50.24; H, 3.98; N, 2.93. Found: C, 50.15; H, 3.46; N, 2.99.

Computational Details. All of the calculations were performed using Gaussian 03 with density function theory, B3LYP functionals, and triple-ζ level basis sets B3LYP/6-311++g**.[11]

Crystal Structure Determinations. Crystals were mounted on glass fibers, and X-ray data were collected on a Bruker AXS SMART CCD diffractometer, using graphite-monochromated Mo Kα radiation (λ = 071073 Å). The program SMART[12] was used for collecting the intensity data, indexing, and determination of lattice parameters. SAINT[12] was used for integration of the intensity reflections and scaling, SADABS[13] for absorption correction, and SHELXTL[14] for space group and structure determination and least-squares refinements against F^2. PLATON[15] was used to locate missing symmetry elements during the process of structure determination. The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for light, non-hydrogen atoms. The hydrogens were placed in calculated positions. Crystallographic data and data collection parameters for **1** and **2** are shown in Table 1.

RESULTS AND DISCUSSION

The synthesis of **1** has been reported by nitration of propionamide using NO_2BF_4.[16] We have tried this methodology following similar procedures[17,18] but with little success. A possible reason could be due to the quality of commercial NO_2BF_4, which tends to be stored over a period of time during which some amounts of HBF_4 could have formed from hydrolysis. The alternative preparation reported here was carried out using the method used to obtain N-nitroacetamide[7] by amidation of propionic anhydride with nitramide (eq 1) to give N-nitropropionamide in low yields (eq 2). The limited spectroscopic data reported for **1** differ somewhat from ours in that the infrared bands are 10−20 cm^{-1} higher than what we observed, even though both are obtained from KBr pellets. The melting points are, however similar, reported[16] as 78 °C, whereas we observe 83 °C. To unambiguously characterize N-nitropropionamide, a single crystal structure was determined. In the solid state, it adopts a crystallographically constrained planar geometry, Figure 1. The N−N bond length in **1** is 0.07 Å longer than in nitramide itself.[19] As shown in the

dx.doi.org/10.1021/ic200090u |*Inorg. Chem.* 2011, 50, 3135–3140

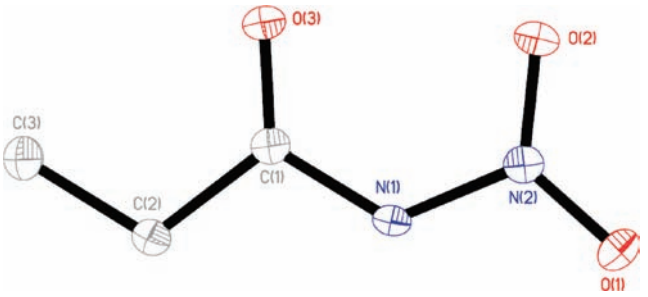


Figure 1. ORTEP plot of **1** drawn to thermal ellipsoid at 50% possibility level.

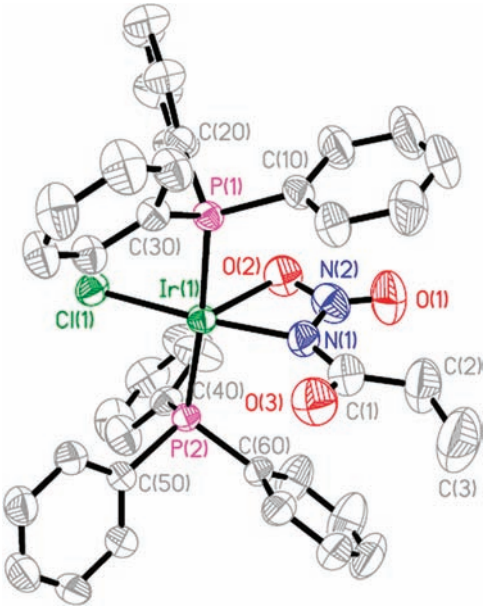
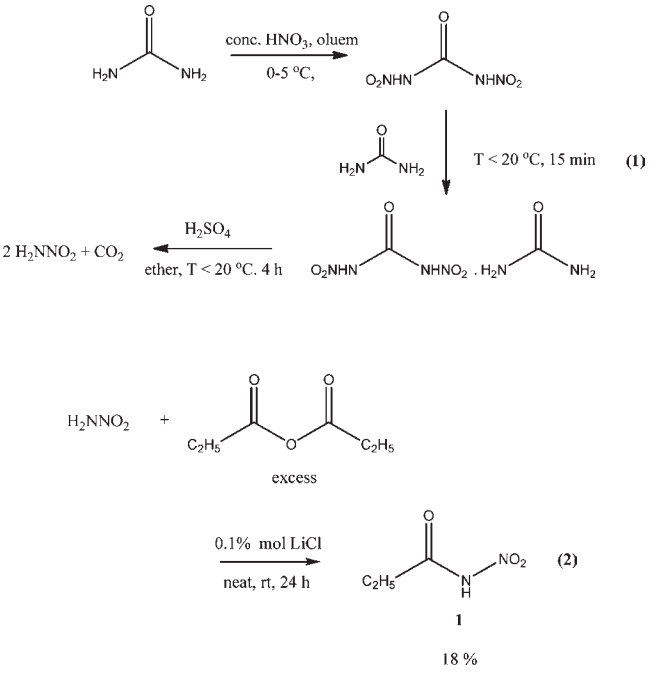


Figure 2. ORTEP plot of **2** drawn to thermal ellipsoid at 50% possibility level. Solvate and hydrogen atoms are omitted for clarity. Key metric parameters not listed in Table 2, (Å) and (deg): Ir(1)−Cl(1) 2.3662(11), Ir(1)−P(1) 2.3315(10), Ir(1)−P(2) 2.3250(10), Cl(1)−Ir(1)−O(2) 111.33(10), and N(1)−Ir(1)−O(2) 59.38(16).

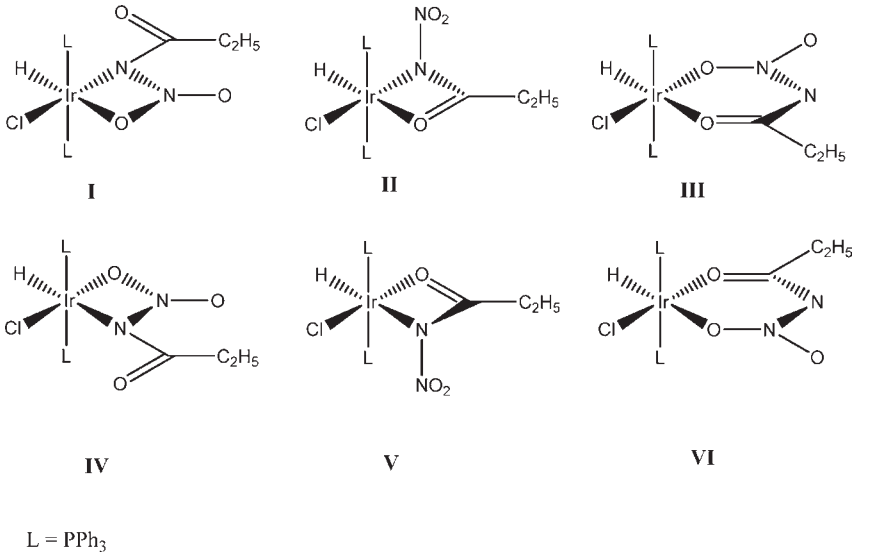
solid state packing diagram in the Supporting Information, the planar N-nitropropionamide molecules are arranged in close hydrogen bound planes with juxtaposed nitro group oxygens. A consequence of acyl oxygen hydrogen bonding to the amide hydrogen is a dense structure with several close contacts, for example, between the nitro groups of adjacent molecules.

The difficulty in synthesizing N-nitroamides arises from their ease of hydrolysis in acidic[17] and strongly basic media. Coupled with the extreme sensitivity of nitramide to basic[20−22] media and to a lesser extent acids,[23,24] the scope for reaction pathways to generate N-nitroamides is very limited.



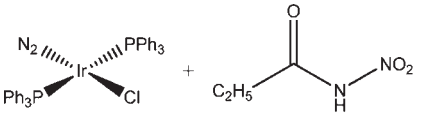
Compound **1** reacts with *trans*-Ir(Cl)(N_2)(PPh_3)$_2$ by oxidatively adding across the amide N−H bond with the concurrent loss of dinitrogen (eq 3). The unusual high acidity of the amidic proton is facilitated by the electron-withdrawing effect of the nitro group on the amide functionality. *trans*-Ir

Scheme 1. Possible Coordination Isomers of 2

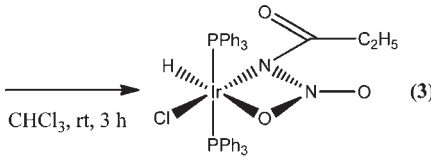


dx.doi.org/10.1021/ic200090u |*Inorg. Chem.* 2011, 50, 3135–3140

$(\eta^2\text{-}C_2H_5C(O)NNO_2)(H)(Cl)(PPh_3)_2$, **2**, has been characterized by NMR, infrared, and Raman absorption; mass spectrometry; and elemental analysis. The single crystal X-ray diffraction (Figure 2) corresponds to a distorted octahedron with *trans*-triphenylphosphines. Not shown in Figure 2 is the dichloromethane solvate, which lies in the plane and is poised so that there is a close C−H···O=C solvate/acyl interaction (Supporting Information). The nitroamide anion is well ordered with well refined positions for the acyl oxygen and ethyl groups.



1



(3)

2

63 %

Complex **2** shows an unexpected bidentate coordination of the N-nitropropionamide anion through the nitrogen on the amide functionality and the oxygen of the nitro group. The N-nitropropionamide forms a four-membered Ir−N−N−O chelate ring. There are six possible bidentate coordination isomers which arise from N−O/O−O chelate, the position of nitrogen/oxygen atom trans to the metal hydride, and the oxygen atom of the nitro/acyl group that is bound to the Ir center (Scheme 1).

The observed mode of coordination is unique for a couple of reasons. The first is that the oxygen on the acyl functionality is not the preferred coordinating site to the Ir center. There are substantially greater numbers of cases of acyl group coordination, e.g., metal-acetylacetonyl ligands (acac), compared to nitro group coordination, as there are only a few examples where

Scheme 2. Coordination Isomers of [Ni(N-nitroacetamide)$(CN)_2$] Used in DFT Calculations

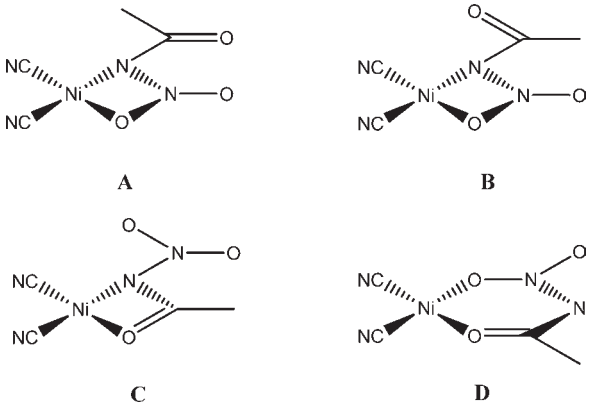


Table 2. Relative Free Energy, Selected Bond Lengths (Å), Bond Angles (deg), and Vibration Modes (cm^{-1}) of 1, 2, A, B, C, and D

	1	2	A	B	C	D
			calculated free energy (A.U.)[a]			
absolute energy (AU)			−2107.4194	−2107.4108	−2107.4085	−2107.4163
relative energy ΔG (kcal mol^{-1})			0	5.9	6.8	1.9
			bond lengths			
N−N	1.3858(18)	1.389(6)	1.34763	1.33406	1.37708	1.35565
N−O[b]	1.2183(16)	1.298(6)	1.29418	1.28629	1.2409	1.2756
	1.2141(16)	1.193(6)	1.20545	1.21990	1.2179	1.2205
C−N	1.3949(19)	1.372(7)	1.40706	1.41290	1.35441	1.34703
C−O	1.2089(17)	1.246(7)	1.21386	1.20934	1.25992	1.25421
M−N		2.042(4)	1.96921	1.97700	1.99173	
M−O[c]		2.357(4)	1.97541	1.99697	2.01772	1.9391
						1.9058
			bond angles			
M−N−N		101.3(3)	92.259	92.468	144.993	
C−N−N	125.27(12)	120.7(4)	121.022	122.269	122.443	119.866
N−N−O[d]	114.40(11)	109.6(4)	108.316	109.372	116.171	124.999
	119.18(11)		128.841	127.970	119.381	116.299
O−N−O	126.42(12)	123.9(5)	122.843	122.618	124.388	118.702
			vibration modes			
v1	1729	1720, 1692	1753.8	1763.62	1598.66	1607.15
v2	1610	1509	1578.7	1550.04	1554.5	1529.58
v3	1140	1168	1236.4	1278.22	1288.96	1188.92
v4	1070	1096	1017.7	1090.24	1106.00	947.19

[a] B3LYP/G-311++G**. [b] Top: coordinated O. Bottom: free O. [c] Top: N−O−Ni. Bottom: C−O−Ni. [d] Top: coordianted O. Bottom: free O.

dx.doi.org/10.1021/ic200090u |*Inorg. Chem.* 2011, 50, 3135–3140

nitro groups coordinate to the transition metal center. Within these reports, the nitro group coordination is through the oxygen of the nitro group.[25−28] Even in examples where nitro groups are present in the ligands, the preferred coordination to the metal centers is through other functional groups.[25,29,30] The second reason is that, between a four- or six-member cyclic structure that can be adopted by the bidentate coordination, a six-membered chelate is usually more favorable. In our case, the anionic N-nitropropionamide takes up a four-member chelate ring.

In trying to assign the observed vibrational spectra and to better understand and determine if the conformation of the observed structural form of **2** is thermodynamically controlled, we embarked on DFT calculations using [Ni(II)(N-nitroacetamide)$(CN)_2$] as a model (Scheme 2). This choice of model allows for a clear separation of nitramide vibration modes from other ligand modes.

A comparison of the computational models between the ligand bound complex and the different coordination isomers, however, shows that the observed structural isomer does not correspond thermodynamically to the most stable one (Table 2). Model **A**, which is the *Z* isomer of **B** (isostructural with **2** for our analysis), is calculated to be thermodynamically the most stable. Model **D**, with a close similarity to acac coordination, is also thermodynamically more stable than **B**. Model **C**, with the acyl oxygen coordination, is the least thermodynamically favorable. We note the generally small energy differences between the different gasphase structures and that the observed solid state geometry is almost certainly affected by the packing associated with the dichloromethane solvate (Supporting Information).

The vibration bands derived from the calculated models correlate well with the experimental data that were obtained, and these are the goal of the calculations: the calculated ν1 mode, which has a large contribution from the C═O stretch in the ligand, and the experiments and theoretical results for **A** and **B**. For **C** and **D**, which have acyl coordination, this mode is predicted to decrease to less than 1610 cm^{-1}, and this band provides an excellent way to distinguish **A** or **B** from **C** or **D.** For ν2 and ν3 modes, which largely originate from the nitro group vibration modes, the calculated values obtained from the models are similar to the experimental data. The pseudoacac, **D**, shows much similarity to even the magnitude of the shift. The vibration mode, ν4, is mostly a compound vibration involving both the nitro and acyl groups in the ligand. The four-membered chelate models have a better fit to **2** compared to **D** for this vibration mode.

CONCLUSION

N-nitropropionamide has been synthesized from an alternate preparation and reacts oxidatively to give *trans*-Ir(η^2-C_2H_5C-(O)NNO_2)(H)(Cl)$(PPh_3)_2$ in good yields. Complex **2** has been characterized and compared with simulated models to gain insight into correlating its vibrational modes with coordination geometry. Additional reactivity studies on **1** and **2** are in progress.

ASSOCIATED CONTENT

Supporting Information. Table with coordinates for the optimized structures **A**−**D**. ^1H and ^{31}P NMR spectra and packing diagrams for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mail: Scott.Bohle@mcgill.ca.

ACKNOWLEDGMENT

We gratefully acknowledge the CRC, CFI, and NSERC for support in the forms of CRC, CFI, and discovery grants to D.S.B.

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