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Synthesis and coordination chemistry of organoiridium complexes supported by an anionic tridentate ligand†

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Treatment of deprotonated *N*-(dimethylaminoethyl)-2-diphenylphosphinoaniline with bis(cyclooctene)iridium chloride dimer affords a thermally stable iridium(I) olefin complex. Infrared analysis of the corresponding monocarbonyl iridium(I) compound indicates a relatively electron rich metal center. Reaction of the iridium(I) cyclooctene complex with iodomethane effects oxidation of the metal yielding a five-coordinate iridium(III) methyl iodide complex which reversibly coordinates tetrahydrofuran. X-ray crystallography confirms coordination of ether to the iridium(III) methyl iodide complex and NMR spectroscopic experiments establish an equilibrium constant of 1.66(9) M for tetrahydrofuran binding. A five-coordinate iridium(III) dimethyl complex has also been prepared and characterized by X-ray diffraction. Hydrogenolysis of the dialkyl species permits identification of a short-lived classical iridium(III) dihydride complex.

Introduction

Platinum group metal complexes supported by tridentate ligands have demonstrated a rich chemistry, promoting such difficult transformations as C–H bond oxidative addition, hydrodesulfurization, carbon dioxide activation, and C–C bond cleavage.[1] A combination of hard and soft donor sites in these chelating ligands has become a common motif which is believed to contribute to their desirable reactivity by attenuating the electronic properties of the metal and, in some cases, offering a hemilabile site for substrate binding.[2] For example, Milstein and coworkers have demonstrated a range of ruthenium catalyzed transformations of alcohols which rely on both a reversible dearomatization of the chelate ligand and the dechelation of a hard amine or pyridine donor *trans* to a soft pendant phosphine ligand.[3] The reactivity of tridentate supported transition metal complexes may also be influenced by the rigidity of the hydrocarbon groups which often link the hard and soft donor sites.[4] Ligands bearing more geometrically restricted aryl bridges typically enforce tight binding of the donor sites, while those with ethane bridges permit more facile dissociation or distortion.[5] These attributes can significantly impact the coordination chemistry of the transition metal complexes bearing tridentate ligands and, in turn, their ability to mediate desirable catalytic processes.

Recently Lee and Liang have described the preparation of the tridentate ligand *N*-(dimethylaminoethyl)-2-diphenylphosphinoaniline (PNN) (Fig. 1) and its coordination to dialkyl aluminium centers.[6] The PNN ligand offers several intriguing features in relation to the vast array of tridentate ligands previously reported,[1,2] including an asymmetric combination of ethane and aryl bridging groups linking a pair of hard amino/amide nitrogens to a soft diphenyl phosphine group. In addition, the small dimethyl amino substituents may be expected to present a more sterically vulnerable metal center than the bulky ^{t}Bu or ^{i}Pr groups commonly used to protect other tridentate transition metal complexes.[1,2] These characteristics motivated our efforts to explore the coordination chemistry of the PNN ligand on a platinum group transition metal and assess the ligand's ability to support reactive transition metal alkyl and hydride species. Herein we present the synthesis and characterization of a series of organoiridium complexes bearing the PNN ligand, and investigations into the coordination chemistry and stability of these compounds.

Experimental

General considerations

All manipulations were carried out using standard vacuum, Schlenk, cannula or glovebox techniques. Argon, nitrogen, and hydrogen were purchased from Corp Brothers and used as received. *N*-(Dimethylaminoethyl)-2-diphenylphosphinoaniline (PNN)[6] and $[Ir(COE)_2Cl]_2$[7] were prepared according to literature procedures. All other chemicals were purchased from Aldrich, VWR, Strem, Fisher Scientific or Cambridge Isotope Laboratories. Volatile, liquid chemicals were dried over 4 Å molecular sieves and distilled prior to use. Solvents were dried and deoxygenated using literature procedures.[8]

^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker DRX 400 Avance and 300 Avance MHz spectrometers. ^1H and ^{13}C

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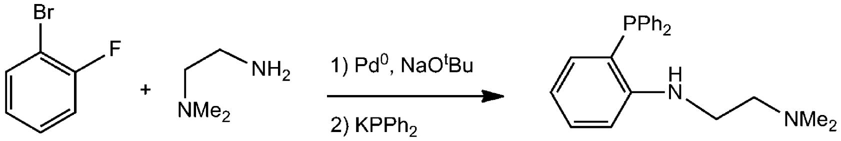

Fig. 1 Lee and Liang's preparation of the PNN ligand.

Table 1 Crystal structure refinement data for (PNN)Ir(CH_3)I(THF) and (PNN)Ir(CH_3)$_2$

Compound	(PNN)Ir(CH_3)I(THF)	(PNN)Ir(CH_3)$_2$
Formula	$C_{27}H_{35}IIrN_2OP$	$C_{24}H_{29}IrN_2P$
M	753.67	568.70
D_{calc}/g cm^{-3}	1.915	1.726
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$Pbca$
a/Å	10.255(5)	15.389(5)
b/Å	16.564(8)	16.679(5)
c/Å	15.548(8)	17.057(5)
α/°	90	90
β/°	98.213(6)	90
γ/°	90	90
V/Å^3	2614(2)	4378(2)
Z	4	8
T/K	173	296
Radiation	Mo Kα 0.71073	Mo Kα 0.71073
$2\theta_{max}$/°	23.250	29.040
F(000)	1456	2232
R_1 ($I > 2\sigma(I)$)	0.0814	0.0477
wR_2 (all data)	0.2393	0.1315

chemical shifts are referenced to residual solvent signals; ^{31}P chemical shifts are referenced to an external standard of H_3PO_4. Probe temperatures were calibrated using ethylene glycol and methanol as previously described.[9] Unless otherwise noted, all NMR spectra were recorded at 23 °C. IR spectra were recorded on Jasco 4100 FTIR and Metler Toledo React IR spectrometers. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Madison, NJ. X-ray crystallographic data were collected on a Bruker Smart Apex I diffractometer. The structures were solved from direct methods and Fourier syntheses and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all non-hydrogen atoms. Crystallographic calculations were carried out using SHELXTL. A summary of crystallographic data is presented in Table 1.

Preparation of {(κ^3-N,N,P)$Me_2N(CH_2CH_2)N$(*o*-$C_6H_4PPh_2$)}-Ir(COE) (1-COE). A 20 mL scintillation vial was charged with 0.145 g (0.161 mmol) of [Ir(COE)$_2$Cl]$_2$ and 10 mL toluene. To this orange solution, 0.114 g (0.322 mmol) of PNNLi in diethyl ether was added (generated from mixing 1 eq. of *N*-(dimethylaminoethyl)-2-diphenylphosphinoaniline and 1eq. *n*-butyl lithium). The resulting orange-brown reaction mixture was stirred for 2 days and subsequently filtered and washed with 5 mL of toluene. The filtrate was collected into a 20 mL scintillation vial and concentrated to a volume of approximately 5 mL toluene. Then 2 mL of pentane was slowly layered on top of the solution and chilled at −35 °C to afford 0.113 g (54%) of orange powder identified as **1-COE**. Anal. Calcd. for $C_{30}H_{38}IrPN_2$: C, 55.45; H, 5.89; N, 4.31. Found: C, 55.61; H, 6.13; N, 4.08. ^{1}H NMR (benzene-d_6): δ 0.99 (m, 4H, COE-CH_2), 1.51 (m, 4H, COE-CH_2), 1.74 (m, 4H, COE-CH_2), 1.94 (d, 6 Hz, 3H, N-CH_3), 2.20 (broad d, 2H, COE-CH), 2.37 (t, 2H, N-CH_2), 3.03 (t, 2H, N–CH_2), 6.44 (m, ArH), 8.13 (m, ArH). ^{31}P {^{1}H} NMR (benzene-d_6): δ 15.21. ^{13}C {^{1}H} NMR (benzene-d_6): δ 27.65 (COE-CH$_2$), 32.47 (COE-CH$_2$), 33.02 (COE-CH$_2$), 47.35 (N–CH$_3$), 47.43 (COE-CH), 49.34 (N–CH$_2$), 69.39 (N–CH$_2$), 108.66, 115.49, 130.00, 131.10, 131.68, 132.34, 132.72, 134.80, 135.45, 135.95 (Ar).

Preparation of {(κ^3-N,N,P)$Me_2N(CH_2CH_2)N$(*o*-$C_6H_4PPh_2$)}-IrCO (1-CO). A 50 mL heavy walled reaction vessel was charged with 0.035 g (0.054 mmol) of **1-COE** dissolved in 10 mL toluene. The solution was frozen at −196 °C, and one atmosphere of CO gas was added to the reaction vessel on a high vacuum line. The reaction was warmed to ambient temperature and left to stir for 25 min during which time the color of the solution changed to yellow. The volatiles were removed *in vacuo* and the resulting residue washed with pentane to afford 0.023 g (74%) of **1-CO** as a yellow powder. ^{1}H NMR (benzene-d_6): δ 2.26 (bs, 2H, N-CH_2), 2.51 (bs, 5 Hz, 6H, N–CH_3), 3.00 (bs, 2H, N–CH_2), 6.42 (m, ArH), 6.52 (m, ArH), 6.99 (m, ArH), 7.01 (m, ArH), 7.26 (m, ArH), 7.98 (m, ArH). ^{31}P {^{1}H} NMR (benzene-d_6): 26.04. ^{13}C NMR (benzene-d_6): 49.91 (N–CH$_2$), 52.76 (N–CH$_3$), 68.01 (N–CH$_2$), 110.30, 114.72, 120.86, 130.48, 133.26, 133.75, 134.60, 135.57, 136.17, 166.50 (Ar), 188.65 (CO). IR (KBr): $\upsilon_{C\equiv O}$ 1916 cm^{-1}. IR (benzene): $\upsilon_{C\equiv O}$ 1922 cm^{-1}. The presence of only one carbonyl ligand was also confirmed by ^{13}CO labeling.

Preparation of {(κ^3-N,N,P)$Me_2N(CH_2CH_2)N$(*o*-$C_6H_4PPh_2$)}-Ir(PPh_3) (1-PPh_3). A heavy walled glass reaction vessel was charged with 0.050 g (0.077 mmol) of **1-COE**, 0.018 g (0.069 mmol) of triphenylphosphine and approximately 10 mL of toluene. The orange solution was heated in the sealed tube at 80 °C for five day. The volatiles were then removed *in vacuo* resulting in a red-orange residue which was washed with pentane and extracted into tetrahydrofuran. The solution was concentrated to approximately 2 mL and chilled to −35 °C overnight to afford 0.048 g (77%) of **1-PPh_3** as a red-orange microcrystalline powder. Anal. Calcd. for $C_{40}H_{39}IrP_2N_2$: C, 59.91; H, 4.90; N, 3.49. Found: C; 59.66; H, 4.83; N, 3.27. ^{1}H NMR (benzene-d_6): δ 2.00 (br, 6H, N–CH_3), 2.55 (t, 2H, N–CH_2), 3.23 (t, 2H, N–CH_2), 6.40 (m, 1H ArH), 6.59 (m, 1H ArH), 6.84–7.01 (m, 16H, ArH), 7.27 (m, 1H ArH), 7.64–7.75 (m, 10H ArH). ^{31}P {^{1}H} NMR (benzene-d_6): δ 22.62 (d, 14.6 Hz), 25.15 (d, 14.6 Hz) ^{13}C {^{1}H} NMR (benzene-d_6): δ 48.76 (N–CH$_2$), 50.62 (N–CH$_3$), 69.88 (N–CH$_2$), 108.07, 112.05, 126.78, 127.85, 128.15, 131.46, 133.13, 133.31, 134.71, 134.21 (Ar). Four Ar peaks could not be located or discerned from other signals.

Preparation of {(κ^3-N,N,P)$Me_2N(CH_2CH_2)N$(*o*-$C_6H_4PPh_2$)}-Ir(CH_3)I (1-MeI). A round bottom flask fitted with a needle valve was charged with 0.103 g (0.159 mmol) of **1-COE** and 15 mL of toluene. On a vacuum line, the solution was frozen at −196 °C and 38 Torr (0.190 mmol) of methyl iodide in a 101 mL calibrated gas bulb was admitted to the vessel. The solution was warmed to room temperature and its color subsequently changed from orange

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to deep green. The volatiles were removed *in vacuo* after one hour and the solid residue washed with pentane to afford 0.0667 g (62%) of **1-MeI** as a deep green powder. Anal. Calcd. for $C_{23}H_{27}IrPN_2I$: C, 40.53; H, 3.99; N, 4.11. Found: C, 40.80; H, 3.85; N, 3.83. ^1H NMR (benzene-d_6): δ 1.64 (d, 11 Hz, 3H, IrCH_3), 2.10 (d, 8 Hz, 3H, NCH_3), 2.68 (d, 8 Hz, 3H, NCH_3), 1.82 (m, 1H, N–CH_2), 2.35 (m, 1H, N–CH_2), 2.85 (m, 1H, N–CH_2), 3.01 (m, 1H, N–CH_2), 6.49–6.57 (m, ArH), 7.30 (m, ArH), 7.93 (m, ArH), 8.11 (m, ArH). ^{31}P {^1H} NMR (benzene-d_6): δ 8.53. ^{13}C {^1H} NMR (benzene-d_6): δ –29.30 (Ir–CH_3), 44.52, 49.10 (N–CH_3), 48.56, 66.34 (N–CH_2), 111.63, 114.90, 126.03, 129.67, 130.19, 130.49, 130.77, 131.04, 132.85, 134.38, 135.05, 135.14, 136.09, 136.69 (Ar).

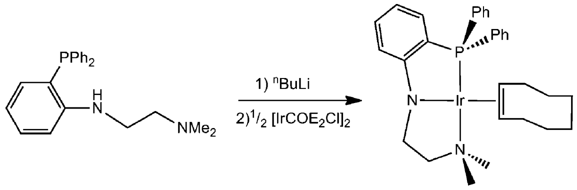
Procedure for determination of equilibrium binding constant of tetrahydrofuran to 1-MeI. In a representative experiment, a J. Young NMR tube was charged with 414 mg of a 0.032 M solution of **1-MeI** in benzene-d_6 and a ferrocene capillary of known concentration. Then 20 equiv. of tetrahydrofuran were added *via* calibrated gas bulb on a high vacuum line at –196 °C. The sample was warmed to 23 °C and monitored by ^1H and ^{31}P {^1H} NMR spectroscopy using sufficient delay times between scans to permit reliable integration of the ferrocene standard and all other ^1H NMR signals. The spectra were monitored over 2 days, but showed no deviation from the data collected directly after THF addition. The relative concentrations of **1-MeI** and (PNN)Ir(CH_3)I(THF) were determined by the position of ^{31}P signal relative to the limiting values of 8.54 and –0.71 ppm, respectively. These were converted to absolute concentrations by accounting for the total moles of iridium complex and the total volume of solvent (benzene-d_6 + tetrahydrofuran) added to the tube. The concentration of free THF was determined by integration of the ^1H NMR signals, and corrected for the amount of (PNN)Ir(CH_3)I(THF) (free and bound THF signals were not resolved). The procedure was repeated for five concentrations of THF.

Preparation of {(κ^3-N,N,P)Me$_2$N(CH$_2$CH$_2$)N(o-C$_6$H$_4$PPh$_2$)}-Ir(CH$_3$)$_2$ (1-Me$_2$). A 20 mL scintillation vial was charged with 0.068 g (0.100 mmol) of **1-MeI** and approximately 10 mL tetrahydrofuran. The green solid quickly produced an orange-yellow solution. Then 7.5 mg (0.140 mmol) of $(CH_3)_2Mg$ was added. The resulting bright orange reaction mixture was stirred overnight, turning to a deep yellow-brown color. The volatiles were subsequently removed *in vacuo* to give an orange solid. The solid was extracted with pentane and filtered through a Pasteur pipette to give a mauve colored solution. Recrystallization at –35 °C afforded 0.027 g (46%) of deep purple crystals identified as **1-Me$_2$**. Further fractions of **1-Me$_2$** may be extracted from the crude reaction residue using diethyl ether, although this material is of diminished purity. Anal. Calcd. for $C_{24}H_{30}IrPN_2$: C, 50.60; H, 5.31; N, 4.92. Found: C, 50.34; H, 5.24; N, 4.78. ^1H NMR (benzene-d_6): δ 1.15 (d, 4 Hz, 6H, Ir–CH_3), 2.08 (d, 5 Hz, 6H, N–CH_3), 2.32 (t, 2H, N–CH_2), 2.99 (t, 2H, N–CH_2), 6.55 (m, ArH), 7.35 (m, ArH), 7.19 (m, ArH), 7.69 (m, ArH). ^{31}P {^1H} NMR (benzene-d_6): δ 12.01. ^{13}C {^1H} NMR (benzene-d_6): δ –17.22 (Ir–CH_3), 47.42 (N–CH_2), 50.09 (N–CH_3), 70.30 (N–CH_2), 110.73, 117.45, 130.02, 131.42, 131.97, 132.49, 133.56, 134.21 (Ar). Two Ar peaks could not be located.

Characterization of {(κ^3-N,N,P) Me$_2$N(CH$_2$CH$_2$)N(o-C$_6$H$_4$PPh$_2$)}Ir(H)$_2$ (1-H$_2$). A J-Young NMR tube was charged with 0.023 g (0.040 mmol) of **1-Me$_2$** dissolved in benzene-d_6. On a high vacuum line, the sample was frozen at –196 °C and one atmosphere of H_2 gas was admitted to the tube. Upon warming the sample, an immediate color change from dark purple to yellow occurred. The product was identified by NMR spectroscopy as **1-H$_2$** formed in virtually quantitative yield. Removal of the excess dihydrogen following hydrogenolysis generally produced sharper signals in the ^1H NMR spectrum. ^1H NMR (benzene-d_6): δ –22.76 (d, 16 Hz, 2H, Ir–H), 2.26 (t, 2H, N–CH_2), 2.53 (d, 5 Hz, 6H, N–CH_3), 3.19 (t, 2H, N–CH_2), 6.58 (m, ArH), 6.98 (m, ArH), 7.94 (m, ArH). ^{31}P {^1H} NMR (benzene-d_6): δ 21.35. ^{13}C {^1H} NMR (benzene-d_6): δ 51.93 (N–CH_2), 54.05 (N–CH_3), 69.12 (N–CH_2), 110.56, 116.82, 130.06, 132.66, 133.90, 134.61, 136.13 (Ar). Three Ar peaks could not be located.

Results and discussion

Coordination of N-(dimethylaminoethyl)-2-diphenylphosphinoaniline to iridium was accomplished by initial deprotonation of the aniline N–H bond with n-butyllithium followed by treatment with bis(cyclooctene)iridium chloride dimer. After stirring for two days at ambient temperature, recrystallization from toluene at –35 °C afforded (PNN)IrCOE (**1-COE**; COE = cyclooctene) in moderate yield (eqn (1)). The orange material was characterized by multinuclear 1D and 2D NMR spectroscopy as well as combustion analysis. The ^1H NMR spectrum of **1-COE** revealed the number of peaks expected for a C_s symmetric complex, including a broad peak at 2.22 ppm and a doublet at 1.94 ppm ($^4J_{P-H}$ = 6.0 Hz) assigned to the vinylic and NMe$_2$ proton, respectively. Additionally two triplet resonances observed at 2.37 and 3.03 ppm were assigned as the methylene sites bridging the nitrogen atoms along the ligand backbone. These assignments, as well as those listed in the Experimental section, were confirmed by a ^1H–^{13}C HSQC NMR experiment. The ^{31}P {^1H} NMR spectrum of **1-COE** displays a single resonance at 15.21 ppm, substantially upfield of the –19.3 ppm chemical shift previously reported for the free ligand, confirming coordination the of chelate.[6]



1-COE

(1)

Cyclooctene complexes of iridium are fairly common given the widespread use of bis(cyclooctene)iridium chloride dimer as a metalation agent.[10] Although such species are most often straightforward olefin adducts with no significant chemical perturbation of the cyclooctene, a few examples of activated iridium–COE compounds have been reported.[11] For **1-COE**, the high symmetry indicated by ^1H and ^{13}C NMR spectra and the absence of a metal–hydride signal are most consistent with simple binding of the alkene within a four-coordinate iridium(I) environment. With a successful protocol for ligation of PNN to iridium in hand, the electrophilicity of the metal center was compared to related complexes by preparation of the iridium(I) monocarbonyl complex, (PNN)IrCO (**1-CO**) (eqn (2)). Addition of one atmosphere of carbon monoxide to **1-COE** resulted in immediate

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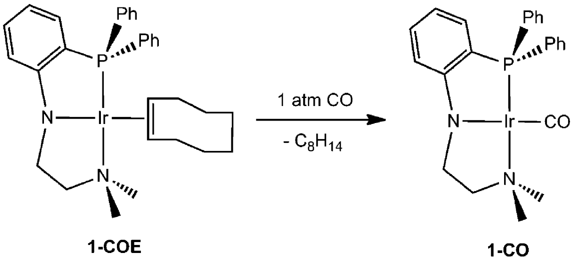
Table 2 Infrared CO stretching frequencies of tridentate ligated iridium(I) carbonyl species

Molecule	*ν*(CO) (cm^{-1})	Ref.
1-CO	1922[a]	This work
	1916[b]	This work
$[(C_6H_3)\text{-}1,3\text{-}(CH_2P^tBu_2)_2]IrCO$	1928[c]	14
$[(C_6H_3)\text{-}1,3\text{-}(OP^tBu_2)_2]IrCO$	1949[c]	14
$[(Ph_2PCH_2SiMe_2)_2N]IrCO$	1930[d]	15
$[(^iPr_2P(C_6H_3Me))_2N]IrCO$	1930[a]	16
$[HB(C_3N_2Me_2H)_3]Ir(CO)_2$	1999.5[b,e]	17

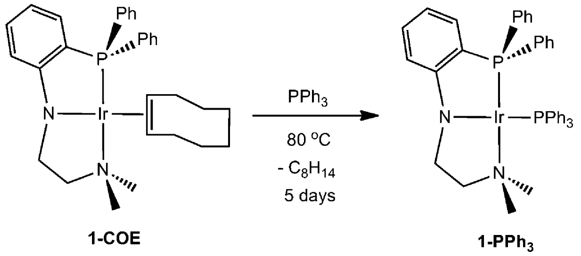
[a] Recorded in benzene. [b] Recorded in KBr. [c] Recorded in pentane. [d] Recorded in dichloromethane. [e] Average frequency.

substitution of the bound olefin, and afforded **1-CO** in good yield upon removal of all volatile material. The monocarbonyl complex was identified by NMR and IR spectroscopy. Significantly, the solution infrared spectrum of **1-CO** exhibits an intense band at 1922 cm^{-1} indicative of a bound carbonyl ligand. This band is slightly lower in energy than carbonyl stretching frequencies observed for similar iridium(I) complexes bearing monoanionic tridentate ligands (Table 2) and suggests the PNN ligand affords a relatively less electrophilic metal center.[12] This trend was somewhat unanticipated as the PNN ligand contains an aryl substituted phosphine group instead of typically more electron donating alkyl substituents. The origin of the red shifted infrared band in **1-CO** may be due to significant π-donation from the anilido nitrogen donor on the chelating ligand (*vide infra*) or alternatively may be an artifact of electrostatic influences on the C–O bond stretching frequency as proposed by Goldman and Krogh–Jespersen for related tridentate iridium carbonyl complexes.[13] In either case, the band at 1922 cm^{-1} for **1-CO** clearly indicates substantial π-backbonding between the iridium center and CO ligand and implies a significant binding energy may be expected for other π-acidic ligands.



(2)

A strong interaction between the (PNN)Ir fragment and cyclooctene is evident in the significant thermostability of **1-COE** which tolerates heating at 150 °C in sealed NMR tubes with benzene-d_6 solvent for hours with no observable decomposition. In fact, even substitution by a strong donor ligand, such as triphenylphosphine, required thermolysis at 80 °C for five days to achieve complete conversion of **1-COE** to (PNN)IrPPh$_3$ (**1-PPh$_3$**) (eqn (3)).[14] However, oxidative substitution of **1-COE** proved considerably more facile. Addition of methyl iodide to **1-COE** at ambient temperature resulted in immediate loss of the cyclooctene ligand and oxidation of the iridium center to yield the deep green complex, (PNN)Ir(CH$_3$)I (**1-MeI**). The five-coordinate iridium(III) methyl iodide product was isolated by filtration from pentane and characterized by multinuclear NMR spectroscopy and combustion analysis. The ^{1}H NMR spectrum of **1-MeI** in benzene-d_6 displayed the number of signals consistent with a C_1 symmetric molecule including doublet resonances at 2.68, 2.10, and 1.64 ppm for the two N–CH$_3$ sites and the Ir–CH$_3$ position, respectively. ^{1}H–^{13}C HSQC NMR spectroscopy indicated a correlation between the proton resonance at 1.64 ppm and an upfield ^{13}C NMR signal at −29.30 ppm, confirming its assignment as the methyl bound to iridium. Additionally, the ^{31}P{^{1}H} NMR spectrum exhibited a singlet at 8.54 ppm, shifted upfield relative to the olefin complex.



(3)

Five-coordinate iridium(III) methyl iodide complexes supported by tridentate ligands have been described previously, and have proven to be valuable precursors for the study of hydrocarbyl reductive elimination reactions, C–P bond formation, and heterolytic dihydrogen activation.[15,19] Fryzuk and coworkers have reported the X-ray structure for a variant supported by the $[N(SiMe_2CH_2P^iPr_2)_2]^-$ ligand which exhibits a generalized square pyramidal geometry.[15] As was observed for the other sterically encumbered tridentate iridium(III) methyl iodide complexes, $[N(SiMe_2CH_2P^iPr_2)_2]Ir(CH_3)I$ appears to require addition of strong, small ligands such as carbon monoxide or primary phosphines, to achieve coordinative saturation.[15,19b] In contrast, the relatively open steric environment of **1-MeI** permits binding of a considerably weaker ligand.

Due to the modest solubility of **1-MeI** in hydrocarbon solvents, initial experiments to assay reactivity were attempted in tetrahydrofuran (THF). Notably, when bright green samples of **1-MeI** were added to THF the solutions immediately became orange. Removal of the THF solvent and redissolving the residue in toluene or benzene resulted in reversal of the solution to the original green color. This behavior suggests a reversible interaction between the cyclic ether and the iridium center. Coordination of THF has been reported in numerous cationic iridium complexes,[20] but isolated examples are rare for neutral compounds[21] presumable due to the reduced electrophilic character of the metal center. Tetrahydrofuran coordination to the iridum(III) methyl iodide species was confirmed by an X-ray diffraction experiment. An orange single crystal sample was obtained by chilling a concentrated THF solution of **1-MeI** at −35 °C for three days. The small crystals produced data of marginal quality, but was successfully refined to obtain the solid state structure of (PNN)Ir(CH$_3$)I(THF) which is presented in Fig. 2.

The data reveal a generalized octahedral geometry about the metal center, with the THF ligand bound *trans* to the iridium–methyl bond. The Ir(1)–O(2) bond length of 2.36(1) Å is comparable (within the low resolution of the structure) to previously reported values for both cationic and neutral iridum–tetrahydrofuran adducts.[20c,21b] Interestingly, the normally strong *trans* influencing methyl ligand does not drastically elongate the iridium–oxygen bond, although it may contribute to weakening the ether adduct (*vide infra*).

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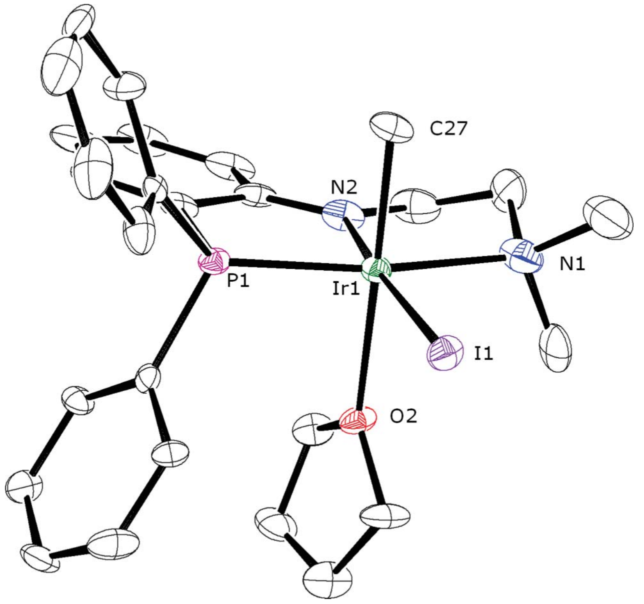

Fig. 2 Molecular structure of (PNN)Ir(CH_3)I(THF) at 30% probability ellipsoids. All hydrogen atoms are omitted for clarity. Select bond distances (Å) and angles (°): Ir(1)–C(27) 2.06(2), Ir(1)–O(2) 2.36(1), Ir(1)–P(1) 2.219(5), Ir(1)–N(1) 2.22(2), Ir(1)–N(2) 2.00(1), Ir(1)–I(1) 2.690(2); C(27)–Ir(1)–O(2) 177.8(6), P(1)–Ir(1)–N(1) 164.4(5), P(1)–Ir(1)–N(2) 84.4(5), N(2)–Ir(1)–N(1) 80.2(7).

The strength of the iridium–tetrahydrofuran interaction was examined by a set of titration experiments. A sample of **1-MeI** in benzene-d_6 was treated progressively with 5, 10, 100, 200, and 600 equivalents of THF. Each successive addition of ether diminished the green hue of the sample and altered the observed chemical shifts in the ^{1}H and ^{31}P{^{1}H} NMR spectra. Changes in the ^{1}H NMR spectra were relatively minor with chemical shift changes of less than 0.6 ppm observed under conditions where the signals were not obscured by added THF. The influence of added THF in the ^{31}P{^{1}H} NMR spectra was more dramatic with a single resonance shifting gradually upfield from 8.53 ppm in the absence of THF down to −0.71 ppm with 600 equivalents of ether. Further additions of THF effected no detectable change in the NMR spectra. Significantly, the observation of a single sharp ^{31}P resonance in the presence of ether is consistent with a rapid and reversible binding of THF to **1-MeI** at ambient temperature, where the chemical shift reflects the relative proportion of (PNN)Ir(CH_3)I and (PNN)Ir(CH_3)I(THF) in a given concentration of THF (Fig. 3).[9]

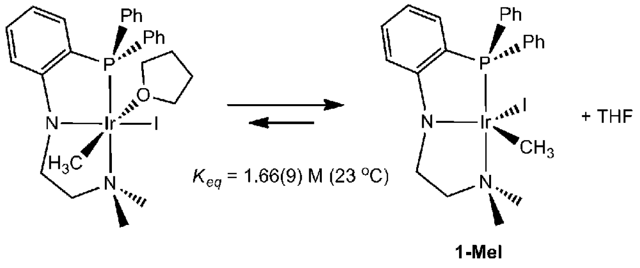

Fig. 3 Reversible coordination of tetrahydrofuran to **1-MeI**.

The equilibrium constant of THF binding was determined from additions of excess cyclic ether to benzene-d_6 solutions of **1-MeI**. The concentrations of THF were determined by ^{1}H NMR integration of the signals for THF *versus* an internal ferrocene standard.[18] The concentrations of (PNN)Ir(CH_3)I and (PNN)Ir(CH_3)I(THF) were obtained from the ^{31}P {^{1}H} NMR chemical shift (with respect to the limiting values of 8.54 and −0.71 ppm) and the total concentration of iridium introduced to the sample.[22] While the observation of only one time averaged ^{31}P NMR signal suggests the reaction approaches equilibrium rapidly, this was confirmed by monitoring the component concentrations over two days which afforded no detectable change. These experiments yielded an equilibrium constant of 1.66(9) M for the reversible binding of THF to **1-MeI** at 23 °C, indicating only a weak coordination of THF. The implication that the PNN ligand imparts a fairly electron rich iridium center (*vide supra*) suggests the ability of **1-MeI** to bind THF is may have a substantial steric component, with the low metal electrophilicity being responsible for the weakness of coordination.

The reversible coordination of THF to **1-MeI** did not prevent further alkylation of the metal center. Addition of a small excess of dimethylmagnesium to **1-MeI** in THF afforded (PNN)Ir(CH_3)$_2$ (**1-Me$_2$**) upon recrystallization from pentane or diethyl ether. The iridium(III) dimethyl complex could also be formed using other methylating agents, such as methyl lithium or methyl magnesium bromide, but these produced lower yields and significant quantities of uncharacterized by-products. The **1-Me$_2$** complex was characterized by single crystal X-ray diffraction, elemental analysis, and NMR spectroscopy. The ^{1}H NMR spectrum of **1-Me$_2$** indicated formation of a C_s symmetric molecule with doublets centered at 2.08 and 1.15 ppm assigned to the N–CH_3 and Ir–CH_3 protons, respectively. The resonance at 1.15 ppm was correlated to a peak at −17.22 ppm in the ^{13}C NMR spectrum by means of ^{1}H–^{13}C HSQC NMR spectroscopy. In addition, a single resonance was observed in the ^{31}P {^{1}H} NMR spectrum at 12.01 ppm.

1-Me$_2$ exhibited limited solubility in pentane, which enabled formation of X-ray quality crystals from concentrated solutions of the hydrocarbon solvent at −35 °C. The molecular structure obtained from these dark purple blocks is depicted in Fig. 4. The iridium(III) dimethyl complex shows a generalized trigonal bipyramid geometry with the diphenylphosphine and dimethylamino groups of the PNN ligand occupying the axial sites and the two iridium–methyls and anilido nitrogen arrayed in equatorial positions. The iridium–carbon bond lengths of 2.074(6) and 2.094(6) Å are similar to the metal–carbon bond distance observed in the THF adduct of **1-MeI**. Notably, the Ir(1)–N(1) distance of 2.003(4) Å is substantially shorter than the 2.190(5) Å bond length found for Ir(1)–N(2). A similar trend can be observed in (PNN)Ir(CH_3)I(THF). The short Ir(1)–N(1) bond length may be due to the localized anionic charge on the central nitrogen, but may also indicate a significant degree of π-donation from the anilido nitrogen to the metal center. In fact, this bond is slightly shorter than the analogous Ir–N bond length reported for [N(SiMe$_2$CH$_2$P^{i}Pr$_2$)$_2$]Ir(CH_3)I (2.079(7) Å).[15] Thus the crystallographic data offers some support for π-donation from the PNN ligand as an influencing factor in the relatively red shifted stretching frequency of **1-CO** (*vide supra*).

Complex **1-Me$_2$** has proven to be considerably less stable than **1-MeI** or **1-COE**. While **1-Me$_2$** will persist in rigorously dry

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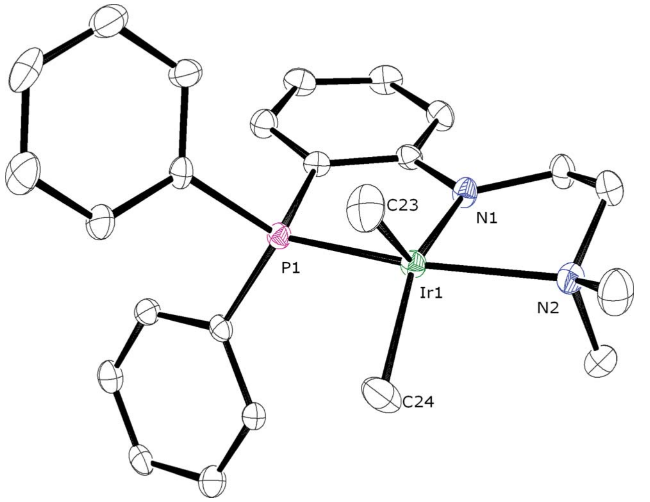

Fig. 4 Molecular structure of **1-Me₂** at 30% probability ellipsoids. All hydrogen atoms are omitted for clarity. Select bond distances (Å) and angles (°): Ir(1)–C(23) 2.074(6), Ir(1)–C(24) 2.094(6), Ir(1)–N(1) 2.003(4), Ir(1)–N(2) 2.190(5), Ir(1)–P(1) 2.202(1); C(23)–Ir(1)–C(24) 77.6(2), P(1)–Ir(1)–N(1) 84.4(1), P(1)–Ir(1)–N(2) 163.4(1), N(2)–Ir(1)–N(1) 79.4(2).

hydrocarbon solutions for approximately two days at ambient temperature, even mild thermolysis at 55 °C induced complete sample degradation over the course of hours. Recent studies have indicated that five-coordinate iridium(III) dialkyl complexes such as **1-Me₂** may be expected to undergo facile C–C bond reductive elimination upon heating.[19c] Such a process would then permit access to a potentially reactive 14-electron, (PNN)Ir fragment. Unfortunately, no ethane was detected by ^{1}H NMR spectroscopy in the mixture of thermolysis products[23] and considerable quantities of metallic particles were observed precipitating from solution. Conducting thermolysis experiments with the exclusion of light also provided similar results. The limited thermal stability of **1-Me₂** then directed investigations toward more mild routes to activate the dimethyl iridium complex.

Iridium alkyl complexes have previously been employed as precursors for hydrogenolysis reactions to prepare reactive iridium–hydride species[24] which are known to mediate C–H bond activation, olefin hydrogenation and hydrosilylation among other reactions.[25] An analogous synthesis was attempted with **1-Me₂** by addition of one atmosphere of dihydrogen at ambient temperature. Hydrogenolysis of **1-Me₂** occurred immediately upon mixing of the gas into solution, bleaching the dark purple color to afford methane and (PNN)IrH$_2$ (**1-H₂**) (Fig. 5).

The iridium(III) dihydride complex was characterized primarily by NMR spectroscopy, as the species degraded over approximately 6 h with or without the presence of excess H$_2$. **1-H₂** could also be formed by addition of dihydrogen to **1-COE**, although this transformation was slow and substantial degradation of the iridium dihydride complex occurred prior to complete consumption of the cyclooctene iridium(I) complex. Interestingly, hydrogenation of the cyclooctene was not detected upon treatment of **1-COE** with H$_2$, instead simple substitution of the olefin was observed by NMR spectroscopy. The ^{1}H NMR spectrum of **1-H₂** in benzene-d_6 indicates a high symmetry structure with an upfield shifted metal–hydride resonance at −22.76 ppm ($^2J_{\text{P–H}}$ = 16 Hz). The ^{31}P{^{1}H} NMR spectrum of **1-H₂** displayed a singlet at 21.35 ppm. The modest lifetime of **1-H₂** also permitted characterization by both one-dimensional ^{13}C{^{1}H} and two-dimensional ^{1}H–^{13}C HSQC NMR spectroscopy.[18]

The identification of **1-H₂** as a classical iridium(III) dihydride complex is supported by the synthesis of the (PNN)IrHD (**1-HD**) isotopologue which was prepared in a manner analogous to the perproteo complex using HD gas. The NMR spectroscopy for **1-HD** indicated a small isotopic perturbation of the ^{31}P chemical shift downfield to 21.47 ppm and an upfield shift of the iridium–hydride resonance to −22.80 ppm. Significantly, the new metal–hydride signal appeared as a broad doublet with a peak width at half height of only 6.7 Hz. This indicates a maximum possible $J_{\text{H–D}}$ coupling constant of ~3.4 Hz, which is roughly an order of magnitude lower than that typically observed in non-classical dihydrogen complexes.[26] This observation, along with the substantial *cis* $^2J_{\text{P–H}}$ = 16 Hz coupling constant, are consistent with the assignment of **1-H₂** as an iridium(III) species.[27]

The limited stability of **1-H₂** has thus far hampered efforts to assay the reactivity of this sterically accessible hydride species. The exact pathways for the degradation of the iridium(III)) dihydride species are unknown to date, but the observation of dark insoluble particles and small amounts of free PNN ligand in the NMR spectra upon loss of **1-H₂** suggest at least some reduction of the metal center. The presence of a basic anilido nitrogen site in the PNN ligand may facilitate chelate loss, as intramolecular iridium–hydride deprotonation has been observed in similar complexes.[19a,24b,28] Additionally, the relatively small substituents on the PNN ligand may permit formation of iridium–hydride aggregate species.[29] These possibilities are the subject of continued investigation.

Concluding remarks

Organoiridium complexes of the anionic, tridentate *N*-(dimethylaminoethyl)-2-diphenylphosphinoaniline ligand have

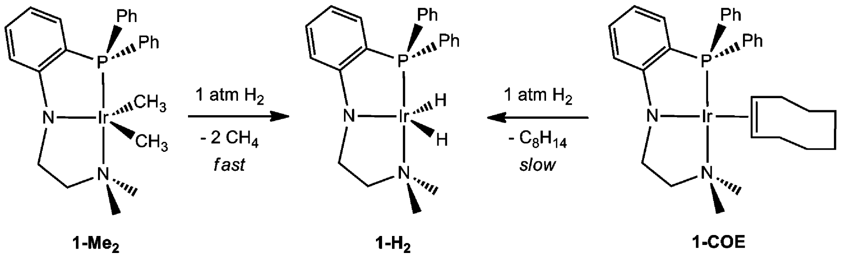

Fig. 5 Synthetic routes for the formation of **1-H₂**.

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been synthesized, representing the first transition metal complexes of this sterically open ligand platform. The combination of hard and soft binding sites supported the formation of a highly stable iridium(I) cyclooctene complex. The chelate ligand imparts an unexpectedly electron rich metal center, as judged by the preparation of the corresponding monocarbonyl complex. The iridium(I) cyclooctene adduct serves as a convenient precursor for preparation of an iridium(III) methyl iodide species, which undergoes reversible coordination of tetrahydrofuran. Binding of the cyclic ether was confirmed by X-ray diffraction, and the equilibrium constant for THF dissociation was determined by NMR spectroscopy. A modestly stable iridum(III) dimethyl complex was prepared by alkylation of (PNN)Ir(CH_3)I and the dark purple compound crystallographically characterized, revealing a trigonal bipyramidal geometry. Hydrogenolysis of (PNN)Ir(CH_3)$_2$ afforded a classical iridium(III) dihydride complex, which was characterized by NMR spectroscopy despite its modest stability. These studies suggest that the open coordination sphere of the *N*-(dimethylaminoethyl)-2-diphenylphosphinoaniline ligand can be used to easily prepare organoiridium complexes as precursors to potentially reactive iridium–hydride species. However, the limited stability of the (PNN)IrH_2 has hindered efforts to further probe its activity. Ongoing investigations are pursing the fate of the (PNN)IrH_2 complex as well as small steric alteration to the PNN ligand to effect enhanced lifetimes of the iridium–hydride species while still maintaining a largely open coordination sphere.

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