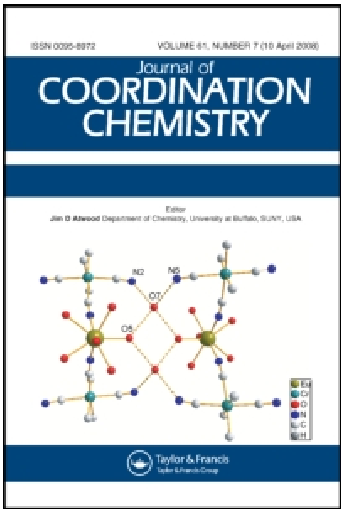
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

IRIDIUM COMPLEXES OF AMPHOS (AMPHOS = [PPh$_2$CH$_2$CH$_2$NMe$_3$]I$^-$): CRYSTAL AND MOLECULAR STRUCTURES OF *trans*-Ir(CO)(Cl)(PPh$_2$CH$_2$CH$_2$NMe$_2$)$_2$ AND [*trans*-Ir(CO)(Cl)(PPh$_2$CH$_2$CH$_2$NMe$_3$)$_2^{2}$][I$^-$]$_2$·2DMSO

Robert L. Rominger[a]; Ronald F. See[a]; Charles H. Lake[a]; Melvyn Rowen Churchill[a]; Jim D. Atwood[a]
[a] Department of Chemistry, University at Buffalo, State University of New York, Buffalo, NY

To cite this Article Rominger, Robert L. , See, Ronald F. , Lake, Charles H. , Churchill, Melvyn Rowen and Atwood, Jim D.(1998) 'IRIDIUM COMPLEXES OF AMPHOS (AMPHOS = [PPh$_2$CH$_2$CH$_2$NMe$_3$]I$^-$): CRYSTAL AND MOLECULAR STRUCTURES OF *trans*-Ir(CO)(Cl)(PPh$_2$CH$_2$CH$_2$NMe$_2$)$_2$ AND [*trans*-Ir(CO)(Cl)(PPh$_2$CH$_2$CH$_2$NMe$_3$)$_2^{2}$][I$^-$]$_2$·2DMSO', Journal of Coordination Chemistry, 46: 2, 165 — 181

To link to this Article: DOI: 10.1080/00958979808053728
URL: http://dx.doi.org/10.1080/00958979808053728

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Coord. Chem., 1998, Vol. 46, pp. 165–181
Reprints available directly from the publisher
Photocopying permitted by license only

© 1998 OPA (Overseas Publishers Association) N.V.
Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

Downloaded At: 15:07 23 January 2011

IRIDIUM COMPLEXES OF AMPHOS (AMPHOS = [PPh$_2$CH$_2$CH$_2$NMe$_3^+$]I$^-$): CRYSTAL AND MOLECULAR STRUCTURES OF *trans*-Ir(CO)(Cl)(PPh$_2$CH$_2$CH$_2$NMe$_2$)$_2$ AND [*trans*-Ir(CO)(Cl) (PPh$_2$CH$_2$CH$_2$NMe$_3$)$_2^{2+}$][I$^-$]$_2$ · 2DMSO

ROBERT L. ROMINGER, RONALD F. SEE,
CHARLES H. LAKE, MELVYN ROWEN CHURCHILL
and JIM D. ATWOOD*

Department of Chemistry, University at Buffalo, State University of New York,
Buffalo, NY 14260-3000

(Received 23 July 1997; Revised 23 July 1997; In final form 24 September 1997)

An improved synthesis of a water-soluble phosphine ligand, PPh$_2$(CH$_2$CH$_2$NMe$_3^+$I$^-$) amphos, is reported. Iridium complexes with amphos, *trans*-Ir(CO)X(amphos)$_2$ (X = Cl, I), Ir(CO)(H)(amphos)$_3$ and Ir(CO)$_3$(amphos)$_2^+$ have been prepared and examined for reactions with H$_2$ and CO. Structures of *trans*-Ir(CO)(Cl)(PPh$_2$CH$_2$CH$_2$NMe$_2$)$_2$ and [*trans*-Ir(CO)(Cl)(PPh$_2$CH$_2$CH$_2$NMe$_3^+$)$_2$][I$^-$]$_2$ · 2DMSO are compared to each other and to *trans*-Ir(CO)(Cl)(PPh$_3$)$_2$. The amphos ligand changes the solubility of iridium complexes, but does not markedly change the nature of the iridium center. Reactions show the effects of more polar solvents.

Keywords: Water soluble; amphos; iridium(I); H$_2$; crystal structure

INTRODUCTION

The last decade has seen growth in studies of organometallic chemistry in water.[1] Use of sulfonated phosphine ligands has been the dominant approach to solubilizing organometallic complexes,[1] although ammonium[2] and phosphonium salts[3] of phosphine ligands have also been used. Amphos,

---

* Corresponding author. E-mail: jatwood@acsu.buffalo.edu. Fax: 716-645-6963.

$[PPh_2CH_2CH_2NMe_3^+]I^-$, was among the first of the water-soluble phosphine ligands prepared,[2] but has not been much examined in the last ten years.

In this manuscript we report an improved synthesis of amphos, synthesis of iridium complexes of amphos, reactions of these complexes in polar solvents and X-ray structural determinations of *trans*-$Ir(CO)(Cl)(PPh_2CH_2CH_2NMe_2)_2$ and *trans*-$[Ir(CO)(Cl)(PPh_2CH_2CH_2NMe_3^+)_2][I^-]_2 \cdot 2DMSO$.

EXPERIMENTAL

Iridium complexes with PPh_3 and $P(p\text{-tolyl})_3$ ligands were prepared as previously described.[4] ^1H and ^{31}P NMR spectra were recorded on a Varian VXR-400 with references set to residual solvent peaks and H_3PO_4, respectively. Infrared spectra were obtained on a Mattson Polaris FTIR with 0.5 mm NaCl, 0.25 mm Irtran solution cells and with KBr disks. Elemental analyses were performed at E&R Microanalytical Laboratory, Inc.

Preparation of $Ph_2PCH_2CH_2NMe_2$

Li ribbon (2.08 g, 0.30 mol) was cut with scissors into small pieces and added to 50 mL THF in a Schlenk flask in a drybox. A second Schlenk flask was used to transport an additional 50 mL dried THF out of the drybox. On a Schlenk line, a three-neck round bottom flask fitted with two gas inlet tubes was purged with $N_2(g)$ and to this was added the Li/THF mixture also under $N_2(g)$. Ph_2PCl (16 g (13 mL), 0.070 mol) was added to the second Schlenk flask containing THF under $N_2(g)$. This mixture was added to a pressure-equalizing dropping funnel and attached to a wing of the three-neck flask.

The Ph_2PCl/THF solution was added dropwise producing a blood red solution of the diphenylphosphide anion. This solution was refluxed two h under $N_2(g)$ and then cooled to room temperature. Remaining Li was removed by rapidly transferring the red solution to another three-neck flask purged with $N_2(g)$ through a wide-neck funnel loosely packed with glass wool.

During reflux in the previous step, an ether solution of $Me_2NCH_2CH_2Cl$ was prepared. $Me_2NCH_2CH_2Cl \cdot HCl$ (10.0 g, 0.070 mol) was mixed with 50 mL of 3.2 M NaOH. Two liquid layers formed. The mixture was separated leaving the top, organic layer in a flask containing anhydrous $MgSO_4$ and the bottom, aqueous layer in the separatory funnel to be extracted three times with dry ether. All extracts were combined with the original organic layer for drying. The aqueous layer was discarded. The ether solution was filtered through a course frit by gravity and the $MgSO_4$ (in the flask and frit) was washed once with 25 mL of dry ether. This wash was also filtered. The combined filtrates were put into a clean dropping funnel.

Downloaded At: 15:07 23 January 2011

Downloaded At: 15:07 23 January 2011

The funnel was placed on one wing of the three-neck flask containing the Ph_2PLi/THF solution. Under N_2(g), the ether solution was added dropwise. The solution turned from deep red to cloudy white. The cloudiness was due to LiCl formation. Any yellow or orange color that may have remained signified incomplete use of Ph_2PLi. The solution was refluxed for one h and then hydrolyzed by adding deaerated H_2O (50 mL) dropwise using an addition funnel. Two liquid layers resulted. The top, organic layer was separated and dried with K_2CO_3. The solution was filtered through a coarse frit by gravity. The drying agent (in flask and frit) was washed once with 25 mL dry ether. The filtrates were combined in a Schlenk flask and solvent was removed *in vacuo*. A cloudy, white, viscous liquid resulted.

The liquid was purified by vacuum distillation (0.1 mm) using a shortpath condenser. Two fractions were collected. The first was collected at temperatures up to 100°C and discarded. The second fraction was collected at 125–130°C. Distillation was stopped and the clear, colorless, oily liquid was kept under N_2(g) until it could be transferred to a drybox for permanent storage. Yields varied between 50 and 63%. ^1H NMR ($CDCl_3$): 7.45 (m, 4H, o-phenyl), 7.25 (m, 6H, p,m-phenyl), 2.40 (m, 4H, methylene), 2.20 (s, 6H, methyl). ^{31}P NMR ($CDCl_3$): -19.80(s). IR(THF): 2313(m), 1952(m), 1886(s), 1814(s), 1762(m), 1661(m). The synthesis of this compound has been previously reported.[2] Literature values: (^1H NMR (neat): 7.35 (m, 10H, phenyl), 2.36 (m, 4H, methylene), 2.10 (s, 6H, methyl). ^{31}P NMR (CH_3OH): -20.5).

Preparation of $Ph_2P(O)CH_2CH_2NMe_2$

$Ph_2PCH_2CH_2NMe_2$ (5.0 g, 0.020 mol) is dissolved in 15 mL deaerated acetone in a Schlenk flask purged with N_2(g). 30% H_2O_2 (2.25 mL, 0.020 mol) solution is added dropwise from a pressure-equalizing addition funnel. The solution is refluxed for one h and cooled to room temperature. Solvent is removed *in vacuo* to reveal a white, pasty solid. Yields varied from 70 to 90%. ^1H NMR ($CDCl_3$): 7.65 (m, 4H, o-phenyl), 7.40 (m, 6H, p,m-phenyl), 2.57 (m, 2H, PCH_2), 2.42 (m, 2H, CH_2N), 2.15 (s, 6H, $N(CH_3)_2$). ^{31}P NMR ($CDCl_3$): 32.7(s). IR(KBr): 1699(m), 1591(m), 1439(s).

Preparation of $[Ph_2P(O)CH_2CH_2NMe_3][I]$

$Ph_2P(O)CH_2CH_2NMe_2$ (7.5 g, 0.028 mol) is dissolved in 40 mL acetone in a Schlenk flask. Pure CH_3I (20 g (8.8 mL), 0.14 mol) is collected from crude CH_3I passed through a column of activated alumina (neutral) and added to the phosphine oxide solution. The entire flask is covered with aluminum foil and the mixture stirred for four h. The resulting white solid is filtered through a medium frit, washed twice with 10 mL acetone and dried *in vacuo*.

Yields obtained were 90 to 95%. Recrystallization is done by dissolving the oxide in a minimum of boiling CH_3CN and allowing it to slowly cool to room temperature. Yields after recrystallization are 38 to 42%. ^1H NMR (D_2O): 7.4–7.8 (m, 10H, phenyl), 3.52 (m, 2H, PCH_2), 3.10 (s + m, 11H, $N(CH_3)_3 + CH_2N$). ^1H NMR (d_6-DMSO): 7.83 (m, 4H, o-phenyl), 7.55 (m, 6H, p,m-phenyl), 3.50 (m, 2H, PCH_2), 3.11 (s + m, 11H, $N(CH_3)_3 + CH_2N$). ^{31}P NMR (D_2O): 38.1(s). ^{31}P NMR (d_6-DMSO): 29.2(s). IR(KBr): 1962(w), 1890(w), 1610(w), 1481(s), 1437(s).

Preparation of [$Ph_2PCH_2CH_2NMe_3$][I]

$Ph_2P(O)CH_2CH_2NMe_3I$ (4.5 g, 0.011 mol) is mixed with 35 mL CH_3CN in a thick-walled sealable reaction vessel in a drybox. The vessel is sealed and brought outside the drybox to a Schlenk line. Under N_2(g), $HSiCl_3$ (5.5 mL (7.4 g), 0.055 mol) is pipetted into the vessel and the container sealed. The mixture is heated to a **gentle** reflux with stirring for 24 h. (*Caution*: Pressure buildup can shatter the vessel). The solution is faintly cloudy during reflux. The setup is cooled to room temperature where it returned to its milky nature. Under a heavy stream of N_2(g), the vessel is carefully opened and purged for 15 min to remove excess silane. The white, cloudy solution is carefully hydrolyzed by dropwise addition of 6.5 mL deaerated H_2O *via* pipette. An additional 5 mL H_2O is added to dilute the thick white solution. The mixture is pipetted from the vessel to a Schlenk filter (with frit) into a Schlenk flask. The solvents are removed *in vacuo* to give a glue-like solid. The crude solid is transferred to a drybox where 25 mL CH_3CN is added and the mixture stirred for two h. A vacuum was used to remove the CH_3CN and its H_2O azeotrope to reveal a dry, white solid. Yield is 80%. The solid could be recrystallized by CH_3CN/Et_2O in an H-tube or by layering pentane on a saturated CH_3CN solution of amphos. ^1H NMR (D_2O): 7.38 (m, 4H, o-phenyl), 7.29 (m, 6H, p,m,-phenyl), 3.19 (m, 2H, CH_2N), 2.90 (s, 9H, $N(CH_3)_3$), 2.50 (m, 2H, PCH_2). ^1H NMR (d_6-DMSO): 7.48 (m, 4H, o-phenyl), 7.40 (m, 6H, p,m-phenyl), 3.36 (m, 2H, CH_2N), 3.06 (s, 9H, $N(CH_3)_3$), 2.60 (m, 2H, PCH_2). ^{31}P NMR (D_2O): −18.5(s). ^{31}P NMR (d_6-DMSO): −19.4(s). The synthesis of this compound has been previously reported.[2] Literature values: (^1H NMR (D_2O): 3.10 (s, 9H, $N(CH_3)_3$). ^{31}P NMR (D_2O): −20.3).[2]

Synthesis of $Ir(CO)(Cl)(PPh_2CH_2CH_2NMe_2)_2$

$Ir(CO)(Cl)(PPh_3)_2$ (0.50 g, 6.4×10^{-4} mol) was dissolved in THF (25 mL) in a Schlenk flask in the drybox. $Ph_2PCH_2CH_2NMe_2$ (0.80 g, 3.1×10^{-3} mol)

Downloaded At: 15:07 23 January 2011

was added to the solution. The mixture was stirred overnight. The color changed from yellow to orange. One half of the volume was removed *in vacuo*. An equal volume of hexane was added. A pale, yellow solid precipitated. The solid was filtered off *via* a fritted funnel and discarded. The solvent was removed from the filtrate *in vacuo*. Hexane (30 mL) was added to the sticky solid. The mixture was stirred overnight. A yellow solid was filtered off using a fritted funnel. Yield was 58%. Crystals suitable for X-ray crystallographic studies were produced in an H-tube using benzene and heptane. ^{1}H NMR ($CDCl_3$): 7.72 (m, 8H, o-phenyl), 7.41 (m, 12H, p,m-phenyl), 2.75 (m, 8H, -PCH_2CH_2N), 2.20 (s, 12H, -$N(CH_3)_2$). ^{31}P NMR ($CDCl_3$): 16.80(s). IR(THF): $\nu_{CO} = 1958$(s). IR(KBr): $\nu_{CO} = 1946$(s).

Synthesis of $[Ir(CO)(Cl)(PPh_2CH_2CH_2NMe_3)_2^{2+}][I^-]_2$

$Ir(CO)(Cl)(PPh_3)_2$ (0.19 g, 2.4×10^{-4} mol) was dissolved in THF (30 mL) in a Schlenk flask in the drybox. $Ph_2PCH_2CH_2NMe_3I$ (0.17 g, 4.3×10^{-4} mol) was added to the solution. The cloudy mixture was stirred overnight. A yellow precipitate was filtered off *via* a fritted funnel. The solid was washed with two 10 mL portions of THF and one 10 mL portion of benzene. Remaining solvent was removed from the solid *in vacuo*. Yield was 73%. Crystals suitable for X-ray crystallographic study were produced from a frozen DMSO/complex solution topped with THF being allowed to warm to room temperature. Crystals (shown later to be the di-DMSO solvate) formed within three d. The solid was somewhat soluble in H_2O but less soluble in D_2O. ^{1}H NMR (d_6-DMSO): 7.81 (m, 8H, o-phenyl), 7.52 (m, 12H, p,m-phenyl), 3.73 (m, 4H, -CH_2N-), 3.32 (m, 4H, -PCH_2-), 3.11 (s, 18H, -$N(CH_3)_3$). ^{31}P NMR (d_6-DMSO): 19.56(s). IR(KBr): $\nu_{CO} = 1974$(s). IR(DMSO): $\nu_{CO} = 1964$(s). Elemental Analysis: calculated %C (39.88), %H (4.40), %Cl(3.36), %I (24.08); experimental %C (40.09), %H (4.45), %Cl (3.61), %I (24.32). If the reactants were allowed to stir for four d or longer the production of $Ir(H)_2(CO)(X)(Ph_2PCH_2CH_2NMe_3I)_2$, where X = I or Cl was seen in very small quantities.

Synthesis of $Ir(CO)(H)(Ph_2PCH_2CH_2NMe_3I)_3$

$Ir(CO)(H)(PPh_3)_3$[5] (0.044 g, 4.4×10^{-5} mol) was dissolved in THF (20 mL) in a Schlenk flask in a drybox. $Ph_2PCH_2CH_2NMe_3I$ (0.053 g, 1.3×10^{-4} mol) was added. The mixture was stirred overnight. A light yellow solid precipitated. The solid was collected *via* a fritted funnel and washed with THF (10 mL) and benzene (10 mL) in succession. ^{1}H NMR (d_6-DMSO): 7.34 (s, 30H, phenyl H's), 3.07 (s, 6H, -PCH_2-), 2.86 (s, 27H, -$N(CH_3)_3$),

Downloaded At: 15:07 23 January 2011

2.71 (s, broad, 6H, -CH_2N-), −11.63 (q, 1H, J = 22, Ir−H). ^{31}P NMR (d_6-DMSO): −3.66(s). IR(KBr): 2048 (s, Ir−H), 1920 (s, CO). Yield was 46%.

Synthesis of $[Ir(CO)_3(Ph_2PCH_2CH_2NMe_3I)_2]ClO_4$

$Ph_2PCH_2CH_2NMe_3I$ (0.100 g, 2.53×10^{-4} mol) was mixed with $[Ir(CO)_3PPh_3)_2]ClO_4$ (0.105 g, 1.09×10^{-4} mol) in THF (15 mL) in a Schlenk flask in the drybox. The solution was stirred overnight. A white solid precipitated. The sample was filtered. The solid was washed two times with benzene (25 mL). The filtrate was discarded. The white solid was analyzed. ^1H NMR(CD_2Cl_2): 7.79 (m, 8H, o-phenyl H's), 7.60 (m, 8H, m-phenyl H's), 7.52 (m, 4H, p-phenyl H's), 3.70 (m, 4H, -CH_2-N) 3.41 (m, 4H, -P-CH_2), 3.17 (s, 18H, -$N(CH_3)_3$). The spectrum showed smaller, broader resonances near the reported ones. The sample may have been a mixture of tricarbonyl cationic species with different counter anions (*i.e.*, I^- or ClO_4^-). ^{31}P NMR(CD_2Cl_2): −9.50(s). IR(KBr): 2050(w), 1994(m), 1940(s). Spectral data corresponded to the product of reaction of $Ir(CO)(Cl)(Ph_2PCH_2CH_2NMe_3I)_2$ with CO(g).

Reactions with H_2

Reactions of *trans*-$Ir(CO)(Cl)(amphos)_2$ and *trans*-$Ir(CO)(I)(amphos)_2$ with H_2 were accomplished on an NMR scale and by a preparative scale. NMR-scale reactions were accomplished on samples ($\sim 5 \times 10^{-5}$ mole) in 1 mL of d_6-DMSO in an NMR tube sealed under 0.78 atm of H_2. Spectra were recorded periodically. Preparative-scale reactions were accomplished on $\sim 9 \times 10^{-5}$ mol samples in 8 mL of H_2O in a Schlenk flask with H_2 passing through the solution overnight. The water was removed and the white solid analyzed by NMR (^1H and ^{31}P) and IR spectra.

X-Ray Diffraction Study on trans-$Ir(CO)Cl(PPh_2CH_2CH_2NMe_2)_2$

A yellow crystal was inserted into a thin-walled glass capillary and aligned on a Siemens R3m/V diffractometer. Determination of Laue symmetry and unit cell dimensions were carried out as described previously.[6] Diffraction data were collected by a coupled 2θ(counter)-θ(crystal) scan technique and were corrected for Lorentz and polarization effects and for absorption. Details appear in Table I.

Crystallographic calculations were carried out under the Siemens' SHELXTL PLUS (Release 4.11) program package[7,8] on a VAXstation 3100 computer. The analytical forms of the scattering factors for neutral atoms were corrected for both the real ($\Delta f'$)[9] and imaginary ($i\Delta f''$) components of

Downloaded At: 15:07 23 January 2011

TABLE I Crystallographic data

	$Ir(CO)Cl(PPh_2CH_2CH_2NMe_2)_2$	$[Ir(CO)Cl(PPh_2CH_2CH_2NMe_3)_2^{2+}][I^-]_2\cdot 2DMSO$
Mol. formula	$C_{33}H_{40}ClIrN_2OP_2$	$C_{39}H_{58}ClI_2IrN_2O_3P_2S_3$
Cryst. syst.	Triclinic	Orthorhombic
Space group	$P\bar{1}$ (No. 2)	$P2_12_12_1$ (No. 19)
a, Å	11.710(1)	12.326(3)
b, Å	12.355(2)	16.208(3)
c, Å	13.615(1)	24.049(7)
α, deg	108.101(8)	90.00
β, deg	113.888(8)	90.00
γ, deg	90.245(9)	90.00
V, Å^3	1692.6(2)	4805(2)
Z	2	4
fw	770.3	1210.4
D(calcd), g/cm^3	1.511	1.673
μ(Mo Kα), mm^{-1}	4.127	4.279
2θ range, deg	5–45°	5–40°
Radiation (λ, Å)	Mo Kα(0.710730)	Mo Kα
Temperature, K	295	298
Index ranges, h	−12 to +12	−11 to 0
k	−13 to +13	0 to +15
l	−14 to +14	−23 to +23
Total reflns.	8839	5024
Independent reflns.	4457 (R_{int} = 1.50%)	4514 (R_{int} = 3.37%)
No. obs. data (> 6σ)	3637	3065
No. parameters refined	393	314
Absolute config., η	Not applicable	+1.06(3)
Weighting scheme, w	$[\sigma^2(F)+0.0011F^2]$	$[\sigma^2(F)+0.0014F^2]$
R (6σ data)	2.52%	3.92%
R_w (6σ data)	3.29%	4.73%
R (all data)	3.63%	7.05%
R_w (all data)	3.81%	5.84%
ρ (min, max), e/Å^3	−0.53, +0.79	−1.63, +1.43 (Near disordered DMSO molecule)

anomalous dispersion.[10] The structure was solved by a combination of direct methods and difference-Fourier syntheses and refinement proceeded smoothly to convergence $[(\Delta/\sigma)_{max} = 0.001]$ with $R = 2.52\%$ for those 3637 independent data with $|F_O| > 6\sigma(|F_O|)$. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in the appropriate idealized trigonal or tetrahedral positions with d(C–H) = 0.96 Å.[11]

X-Ray Diffraction Study of *$[Ir(CO)Cl(PPh_2CH_2CH_2NMe_3)_2^{2+}][I^-]_2\cdot 2DMSO$*

This study followed the process outlined above. Crystallographic data are provided in Table I. The following items should be noted.

Downloaded At: 15:07 23 January 2011

Downloaded At: 15:07 23 January 2011

(1) Data were substantially weaker than for the previous compound. This is probably due to the presence (or even partial loss) of DMSO of crystallization.

(2) The crystallographic asymmetric unit contains one $[Ir(CO)Cl(PPh_2CH_2CH_2NMe_3)^{2+}]$ cation, two independent I^- anions, one ordered DMSO molecule and one disordered DMSO molecule. The $IrCl(P)_2$ moiety, the iodide ions, the oxygen of the CO ligand, the terminal $N(C)_3$ systems and the $(C)_2SO$ atoms of the ordered DMSO molecule were refined anisotropically. All other non-hydrogen atoms were refined isotropically, in order to avoid an unacceptably low data-to-parameter ratio. Hydrogen atoms (save for those of the disordered DMSO molecule) were included in idealized positions. Refinement proceeded rather slowly to convergence $[(\Delta/\sigma)_{max} = 0.001]$ with $R = 3.92\%$ for those 3065 *point-group* independent data with $|F_0| > 6\sigma(|F_0|)$.

(3) This species crystallizes into the noncentrosymmetric space group $P2_12_12_1$. The correct hand for the crystal was determined by η-refinement,[12] yielding $\eta = +1.06(3)$. Although bond lengths are not greatly affected by the choice of crystal chirality (since it is not monopolar),[13] the large $\Delta f'$ and $\Delta f''$ values for the heavy atoms (in units of electrons, $\Delta f' = -2.066$ and $\Delta f'' = 7.990$ for Ir, $\Delta f' = -0.684$ and $\Delta f'' = 1.958$ for I) result in substantial increases in R-factors for the "wrong-handed" model. Thus, a value of $\eta = -1.00$ yields $R = 6.60\%$ for those 3065 data above 6σ and $R = 9.75\%$ for all 4515 data (*cf.* 3.92% and 7.05%, respectively, for the correct model).

(4) The largest ten peaks and troughs in the final difference-Fourier map are all in the vicinity of the disordered DMSO molecule. The remainder of the map is relatively clean.

RESULTS AND DISCUSSION

Amphos $(PPh_2(CH_2CH_2NMe_3^+)I^-)$, a cationic analogue of PPh_3, is prepared from the following five-step sequence:

$PPh_2Cl + 2Li \rightarrow LiPPh_2 + LiCl$

$LiPPh_2 + Me_2NCH_2CH_2Cl \rightarrow PPh_2CH_2CH_2NMe_2$ 60%

$PPh_2CH_2CH_2NMe_2 + H_2O_2 \rightarrow P(O)Ph_2CH_2CH_2NMe_2 + H_2O$ 80%

$P(O)Ph_2CH_2CH_2NMe_2 + CH_3I \rightarrow [P(O)Ph_2CH_2CH_2NMe_3]I$ 90%

$[P(O)Ph_2CH_2CH_2NMe_3]I + HSiCl_3 \rightarrow [PPh_2CH_2CH_2NMe_3]I + HOSiCl_3$ 80%

Downloaded At: 15:07 23 January 2011

The five-step approach was originally reported by Baird and Smith.[2] The last step, however, was difficult to reproduce. Using a sealed flask allows synthesis in overall 35% yield from PPh_2Cl.

Iridium complexes of amphos are prepared by reacting PPh_3 complexes with amphos in THF,

$$\begin{aligned} &\textit{trans}\text{-}Ir(CO)(Cl)(PPh_3)_2 + 2\,\text{amphos} \\ &\quad\rightarrow \textit{trans}\text{-}Ir(CO)(Cl)(\text{amphos})_2(\downarrow) + 2PPh_3 \end{aligned}$$

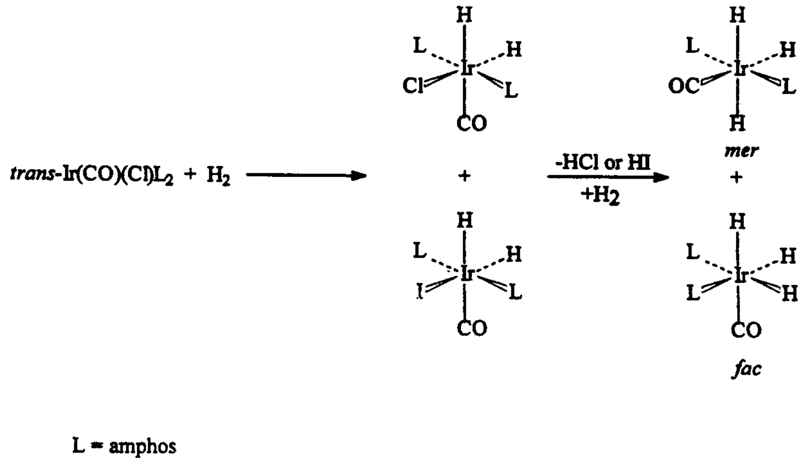
where the amphos complex precipitates. Table II summarizes the iridium amphos complexes prepared and characterization data. The characterization data are remarkably similar to the PPh_3 analogues. Comparison of the three complexes, *trans*-$Ir(CO)(Cl)(PPh_3)_2$, *trans*-$Ir(CO)(Cl)(PPh_2CH_2CH_2NMe_2)_2$ and *trans*-$Ir(CO)(Cl)(\text{amphos})_2$ shows that the use of the water-soluble ligand does not significantly affect the iridium center.

The amphos complexes are sparingly soluble in H_2O, not sufficiently soluble in D_2O for routine NMR analysis. Thus the reactions have been examined in DMSO. Reaction of *trans*-$Ir(CO)(Cl)(\text{amphos})_2$ with H_2 produces four separate products. As studied extensively for other phosphine ligands, H_2 addition occurs to the square-planar complex. However, in a complication for amphos complexes, the Cl^- on iridium and the I^- on amphos exchange giving two separate dihydride complexes (Scheme 1). The hydride portion of the ^1H spectrum is shown in Figure 1, with the $Ir(CO)(Cl)(H)_2(\text{amphos})_2$ resonances at −8.7(dt) and −19.0(dt) ppm and the $Ir(CO)(I)(H)_2(\text{amphos})_2$ resonances at −10.3(dt) and −16.4(dt) ppm. Elimination of HX produces the *fac*- and *mer*-mixture of $Ir(CO)(H)_3(\text{amphos})_2$. Table III shows the full assignments of the hydride region which are in agreement with the PPh_3 and PMe_3 analogues.[14,15] When *trans*-$Ir(CO)(I)(\text{amphos})_2$ is reacted with H_2 only one set of hydride resonances

TABLE II Infrared (ν_{CO}) and ^{31}P characterizations of amphos complexes

Complex	ν_{CO} *(KBr)*	^{31}P*(DMSO)*
Amphos		−19.4
trans-$Ir(CO)(Cl)(\text{amphos})_2$	1974	19.6
trans-$Ir(CO)(I)(\text{amphos})_2$	1960	12.9
$Ir(CO)(H)(\text{amphos})_3$	1920	−3.7
$Ir(CO)_3(\text{amphos})_2^+$	2050(w), 1994(m)	−9.5[a]
$Ir(CO)(Cl)(H)_2(\text{amphos})_2$	1994[b]	0.0
$Ir(CO)(I)(H)_2(\text{amphos})_2$	1994[c]	−5.9
mer-$Ir(CO)(H)_3(\text{amphos})_2$		17.1
fac-$Ir(CO)(H)_3(\text{amphos})_2$		4.9

[a] CD_2Cl_2; [b] ν_{Ir-H} at 2179(w) and 2093(s); [c] ν_{Ir-H} at 2178(w) and 2093(s).



SCHEME 1

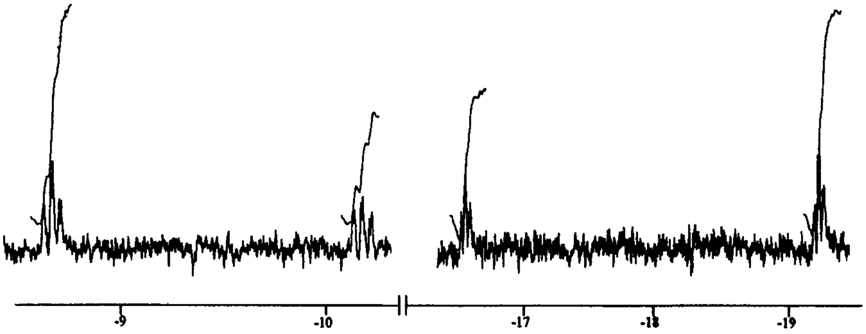


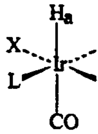
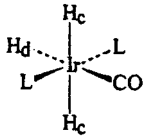
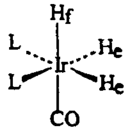
FIGURE 1 Hydride portion of the ^1H NMR for reaction of H_2 with *trans*-Ir(CO)(Cl)-(amphos)$_2$ showing the triplets of doublets for Ir(CO)(Cl)(H)$_2$(amphos)$_2$ and Ir(CO)(I)-(H)$_2$(amphos)$_2$.

(−10.3 and −16.4 ppm) are observed. Since we see no evidence for exchange of the I^- on amphos with the Ir–Cl in the square-planar complex it is likely that the exchange occurs in the six-coordinate dihydride. The X group has been shown to be labile in polar solvents in such six-coordinate dihydride complexes.[16]

Reaction of *trans*-Ir(CO)(Cl)(amphos)$_2$ with CO in DMSO produces Ir(CO)$_3$(amphos)$_2^+$, characterized by comparison of IR and ^{31}P NMR data to independently prepared Ir(CO)$_3$(amphos)$_2^+$. In H_2O a similar reaction was observed but complicated by water gas shift reactions occurring concurrently.

Downloaded At: 15:07 23 January 2011

TABLE III Hydride assignments for the products of H_2 reacting with *trans*-Ir(CO)(Cl)(amphos)$_2$ in DMSO

	X = Cl H_a(dt) at −8.7 ppm (J_{P-H} = 18.4, J_{H-H} = 4.6 Hz) H_b(dt) at −19.0 ppm (J_{P-H} = 13.6, J_{H-H} = 4.6 Hz) X = I H_a(dt) at −10.3 ppm (J_{P-H} = 18.4, J_{H-H} = 4.6 Hz) H_b(dt) at −16.4 ppm (J_{P-H} = 13.6, J_{H-H} = 4.6 Hz)
	H_c(dt) at −10.8 ppm (J_{P-H} = 18.4, J_{H-H} = 4.6 Hz) H_d(tt) at −11.8 ppm (J_{P-H} = 20.2, J_{H-H} = 5.0 Hz)
	H_e, $H_{e'}$ (2nd order multiplet) at −11.8 H_f(t) at −11.0 (J_{P-H} = 19 Hz)

L = amphos.

Downloaded At: 15:07 23 January 2011

Description of the Crystal Structure of trans-Ir(CO)Cl(PPh$_2$CH$_2$CH$_2$NMe$_2$)$_2$

This complex crystallizes in an ordered array as discrete molecular units with no abnormally short intermolecular contacts. Figure 2 illustrates the molecular geometry, while Table IV lists the important interatomic distances and angles. The d^8 iridium(I) center has a slightly distorted square-planar geometry with Ir(1)–P(1) = 2.310(2), Ir(1)–P(2) = 2.321(2), Ir(1)–Cl(1) = 2.346(2) and Ir(1)–CO = 1.802(8) Å. The P(1)–Ir(1)–P(2) angle is 174.5(1)° and the Cl(1)–Ir(1)–C(1) angle is 176.1(2)°; the remaining *cis* angles of 89.1(1)–91.1(3)° are close to the idealized value of 90.0°. These results are in accordance with previous structural studies of *trans*-Ir(CO)Cl[P(*p*-tolyl)$_3$]$_2$[17] (Ir–P = 2.330(2) and 2.332(2) Å, Ir–Cl = 2.364(2) Å, Ir–CO = 1.817(8) Å and (P–Ir–P = 175.19(6)°) and *trans*-Ir(CO)Cl(PPh$_3$)$_2$[18] (Ir–P = 2.330(1) Å; other distances are less accurate due to CO/Cl disorder).

The nitrogen atoms have a clearly pyramidal geometry – angles about N(1) being 109.1(8)–111.4(7)° and those about N(2) being 110.7(5)–113.0(7)°.

The P–$CH_2CH_2NMe_2$ bondlengths, P(1)–C(11) = 1.826(8) Å and P(2)–C(21) = 1.820(6) Å, appear to be slightly shorter than the P–Ph distances (1.832(5)–1.840(6) Å). The angles about phosphorus show the usual pattern of distortions from the ideal tetrahedral value of 109.5° toward a pattern of C_{3v} symmetry, with increased M–P–C angles (Ir–P–C = 109.3(2)–119.3(3)°) and reduced C–P–C angles (100.0(3)–104.9(3)°).

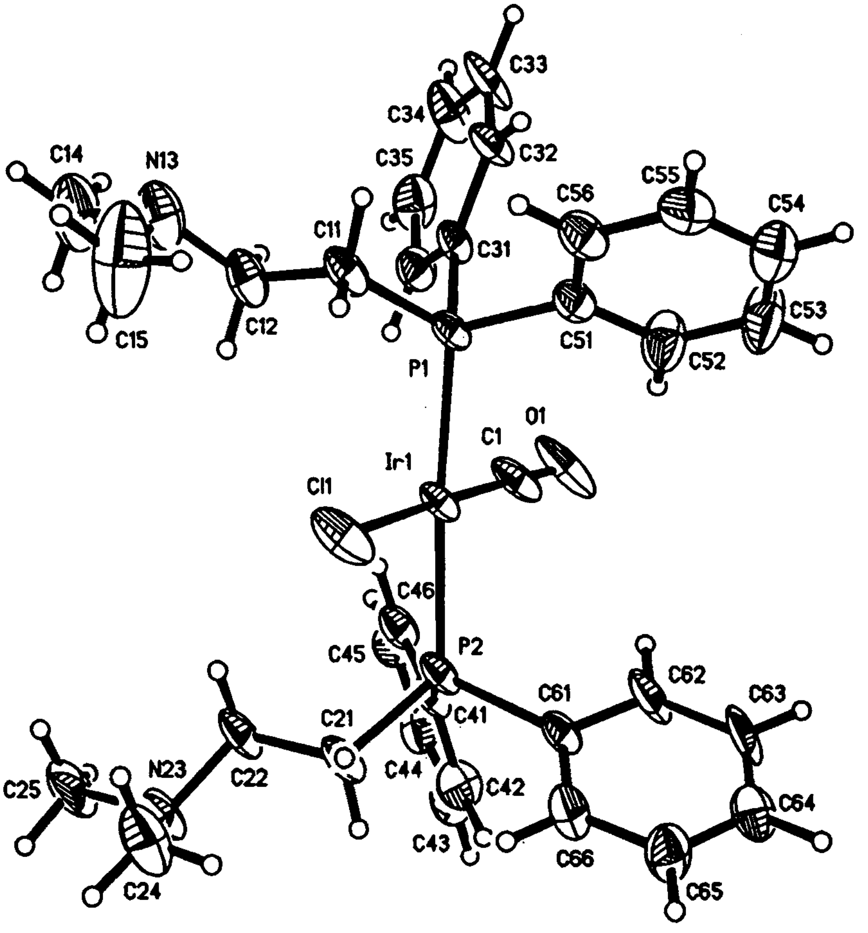


FIGURE 2 Molecular geometry of *trans*-Ir(CO)Cl(PPh$_2$CH$_2$CH$_2$NMe$_2$)$_2$. [ORTEP2 diagram; 30% probability ellipsoids, with hydrogen atoms artificially reduced.]

Description of the Crystal Structure of [trans-Ir(CO)Cl(PPh$_2$CH$_2$CH$_2$NMe$_3$)$_2^{2+}$][I$^-$]$_2$·2DMSO

This complex crystallizes with one ordered dication, two ordered iodide anions, one ordered DMSO molecule and one *disordered* DMSO molecule in the asymmetric unit. Figure 3 shows the packing as viewed down '*a*'. There is an extensive network of hydrogen bonding (C–H···I interactions) around the iodide ions and also C–H···O(sulfoxide) and Cl···H–C(sulfoxide) interactions. The pattern of disorder for the DMSO molecule is such

Downloaded At: 15:07 23 January 2011

TABLE IV Selected interatomic distances (Å) and angles (deg.) for *trans*-Ir(CO)Cl(PPh$_2$CH$_2$CH$_2$NMe$_2$)$_2$

(A) *Distances within Ir(CO)Cl(P)$_2$ core*			
Ir(1)–P(1)	2.310(2)	Ir(1)–P(2)	2.321(2)
Ir(1)–Cl(1)	2.346(2)	Ir(1)–C(1)	1.802(8)
C(1)–O(1)	1.153(10)		
(B) *P–C distances*			
P(1)–C(11)	1.826(8)	P(2)–C(21)	1.820(6)
P(1)–C(31)	1.832(5)	P(2)–C(41)	1.832(7)
P(1)–C(51)	1.836(7)	P(2)–C(61)	1.840(6)
(C) *Distances within CH$_2$CH$_2$NMe$_2$ fragments*			
C(11)–C(12)	1.515(10)	C(21)–C(22)	1.499(9)
C(12)–N(13)	1.468(12)	C(22)–N(23)	1.447(8)
N(13)–C(14)	1.456(11)	N(23)–C(24)	1.454(10)
N(13)–C(15)	1.446(10)	N(23)–C(25)	1.431(10)
(D) *Angles around iridium atom*			
P(1)–Ir(1)–P(2)	174.5(1)	P(1)–Ir(1)–Cl(1)	89.1(1)
P(2)–Ir(1)–Cl(1)	89.8(1)	P(1)–Ir(1)–C(1)	91.1(3)
P(2)–Ir(1)–C(1)	89.7(3)	Cl(1)–Ir(1)–C(1)	176.1(2)
Ir(1)–C(1)–O(1)	178.0(6)		
(E) *Angles around phosphorus atoms*			
Ir(1)–P(1)–C(11)	117.9(2)	C(11)–P(1)–C(31)	100.0(3)
Ir(1)–P(1)–C(31)	117.6(3)	C(11)–P(1)–C(51)	105.5(3)
Ir(1)–P(1)–C(51)	111.2(2)	C(31)–P(1)–C(51)	102.8(3)
Ir(1)–P(2)–C(21)	119.3(3)	C(21)–P(2)–C(41)	102.9(3)
Ir(1)–P(2)–C(41)	115.2(2)	C(21)–P(2)–C(61)	103.8(3)
Ir(1)–P(2)–C(61)	109.3(2)	C(41)–P(2)–C(61)	104.9(3)
(F) *Angles around nitrogen atoms*			
C(12)–N(13)–C(14)	109.1(8)	C(22)–N(23)–C(24)	113.0(7)
C(12)–N(13)–C(15)	111.4(7)	C(22)–N(23)–C(25)	110.7(5)
C(14)–N(13)–C(15)	109.9(8)	C(24)–N(23)–C(25)	111.5(7)

that two separate images of relative occupancies 0.595(18) and 0.405(18) (and with S(2S)···S(2SA) = 1.445(26) Å) with the two alternative sulfur atoms sharing a common carbon and oxygen atom; however each has a separate non-shared carbon atom.

Parameters derived from this structural study are substantially less accurate than for that above for a number of reasons: (1) data were collected to a lower value of 2θ and are weaker; (2) the present structure contains two additional heavy atoms (I$^-$) and a disordered DMSO molecule of crystallization; (3) full anisotropic refinement was deemed unwise due to the low data-to-parameter ratio which would necessarily ensue.

Interatomic distances and angles are collected in Table V. Figure 4 provides a view of the [*trans*-Ir(CO)Cl(PPh$_2$CH$_2$CH$_2$NMe$_3$)$_2^{2+}$] cation. The iridium(I) center is associated with the bondlengths Ir(1)–P(1) = 2.327(5),

Downloaded At: 15:07 23 January 2011

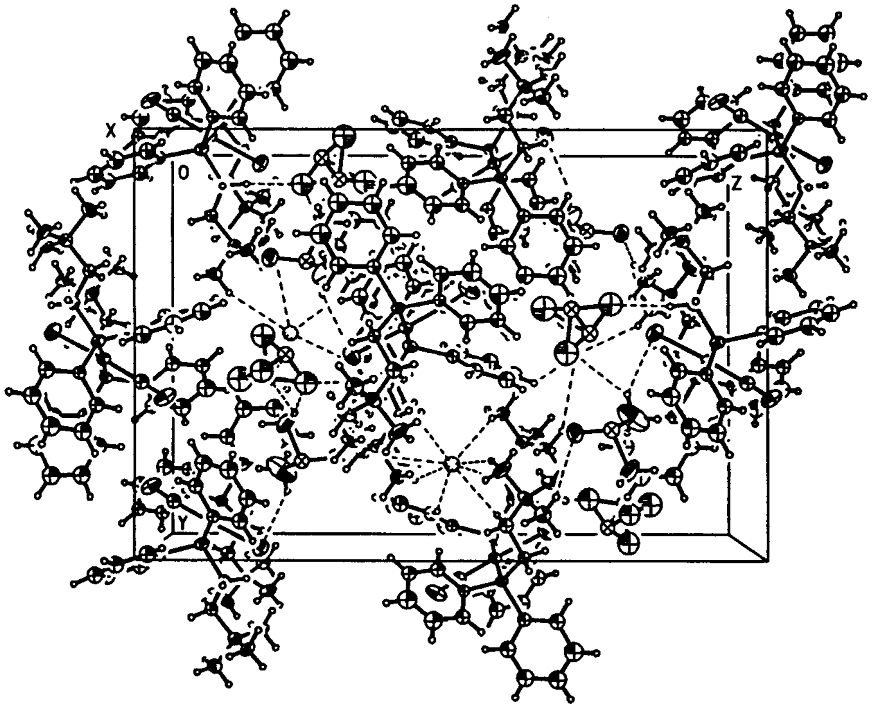


FIGURE 3 Packing diagram for [*trans*-Ir(CO)Cl(PPh$_2$CH$_2$CH$_2$NMe$_3$)$^{2+}$][I$^-$]$_2$·2DMSO, reviewed down '*a*' and showing the extensive C–H···I hydrogen bonding scheme about the I$^-$ ions. [ORTEP2 diagram, 30% ellipsoids, with hydrogen atoms reduced; I$^-$ ions are shown as shaded circles and sulfur atoms (of the DMSO molecules) as diagonally-crossed circles.]

Downloaded At: 15:07 23 January 2011

Ir(1)–P(2) = 2.313(5), Ir(1)–Cl(1) = 2.376(5) and Ir(1)–C(1) = 1.770(21) Å. (The Ir–Cl distance is 0.030(5) Å longer than in the previous complex. We are, however, reluctant to accept this as definitive because of the possibility that it is an artifact caused by some minor exchange of Cl$^-$ by I$^-$ ion at this site – *cf.* Ref. 19).

The nitrogen atoms are quarternary ammonium salts – angles about N(1) are 106.3(13)–111.5(15)° and about N(2) are 107.7(15)–111.5(14)°. The N–C distances within the present quaternary ammonium salts range from 1.447(25) to 1.540(22) Å, averaging 1.496 Å (as opposed to the C–N values of 1.431(10)–1.468(12) Å, averaging 1.450 Å, in the -CH$_2$CH$_2$NMe$_2$ arms of the previously described amine complex). Other distances and angles in this species are normal.

TABLE V Selected interatomic distances (Å) and angles (deg.) for [*trans*-Ir(CO) Cl(PPh$_2$-CH$_2$CH$_2$NMe$_3$)$_2^{2+}$][I$^-$]$_2$ · 2DMSO

(A) *Distances within Ir(CO)Cl(P)$_2$ core*			
Ir(1)–P(1)	2.327(5)	Ir(1)–P(2)	2.313(5)
Ir(1)–Cl(1)	2.376(5)	Ir(1)–C(1)	1.770(21)
C(1)–O(1)	1.129(26)		
(B) *P–C distances*			
P(1)–C(11)	1.783(17)	P(2)–C(41)	1.827(17)
P(1)–C(21)	1.824(18)	P(2)–C(51)	1.797(19)
P(1)–C(31)	1.823(18)	P(2)–C(43)	1.829(17)
(C) *Distances within CH$_2$CH$_2$NMe$_3^+$ fragments*			
C(31)–C(32)	1.469(23)	C(61)–C(62)	1.491(23)
C(32)–N(1)	1.540(22)	C(62)–N(2)	1.491(23)
N(1)–C(33)	1.483(25)	N(2)–C(63)	1.494(26)
N(1)–C(34)	1.475(25)	N(2)–C(64)	1.447(25)
N(1)–C(35)	1.513(24)	N(2)–C(65)	1.528(23)
(D) *Distances in ordered DMSO molecule*			
S(1S)–O(1S)	1.487(16)	S(1S)–C(1S)	1.730(28)
S(1S)–C(2S)	1.768(29)		
(E) *Angles around iridium atom*			
P(1)–Ir(1)–P(2)	177.1(2)	P(1)–Ir(1)–Cl(1)	90.5(2)
P(2)–Ir(1)–Cl(1)	87.7(2)	P(1)–Ir(1)–C(1)	89.8(7)
P(2)–Ir(1)–C(1)	91.9(7)	Cl(1)–Ir(1)–C(1)	177.1(7)
(F) *Angles around phosphorus atoms*			
Ir(1)–P(1)–C(11)	114.1(6)	C(11)–P(1)–C(21)	103.3(8)
Ir(1)–P(1)–C(21)	114.8(6)	C(11)–P(1)–C(31)	104.1(8)
Ir(1)–P(1)–C(31)	115.8(6)	C(21)–P(1)–C(31)	103.2(8)
Ir(1)–P(2)–C(41)	116.0(6)	C(41)–P(2)–C(51)	106.3(8)
Ir(1)–P(2)–C(51)	112.2(6)	C(41)–P(2)–C(61)	100.3(8)
Ir(1)–P(2)–C(61)	117.5(6)	C(51)–P(2)–C(61)	103.0(8)
(G) *Angles around nitrogen atoms*			
C(32)–N(1)–C(33)	110.6(13)	C(62)–N(2)–C(63)	110.0(15)
C(32)–N(1)–C(34)	110.0(14)	C(62)–N(2)–C(64)	111.5(14)
C(32)–N(1)–C(35)	106.3(13)	C(62)–N(2)–C(65)	109.4(13)
C(33)–N(1)–C(34)	111.5(15)	C(63)–N(2)–C(64)	107.7(15)
C(33)–N(1)–C(35)	109.1(15)	C(63)–N(2)–C(65)	109.1(14)
C(34)–N(1)–C(35)	109.2(14)	C(64)–N(2)–C(65)	109.1(15)
(H) *Angles within ordered DMSO molecule*			
O(1S)–S(1S)–C(1S)	108.8(12)	C(1S)–S(1S)–C(2S)	95.8(16)
O(1S)–S(1S)–C(2S)	107.6(13)		

CONCLUSION

Amphos complexes of iridium can be prepared analogously to those for PPh$_3$. The NMR and IR characterization and X-ray crystallography indicate that the ammonium group does not significantly affect properties other than solubility. Reactions of the iridium complexes show elimination of

Downloaded At: 15:07 23 January 2011

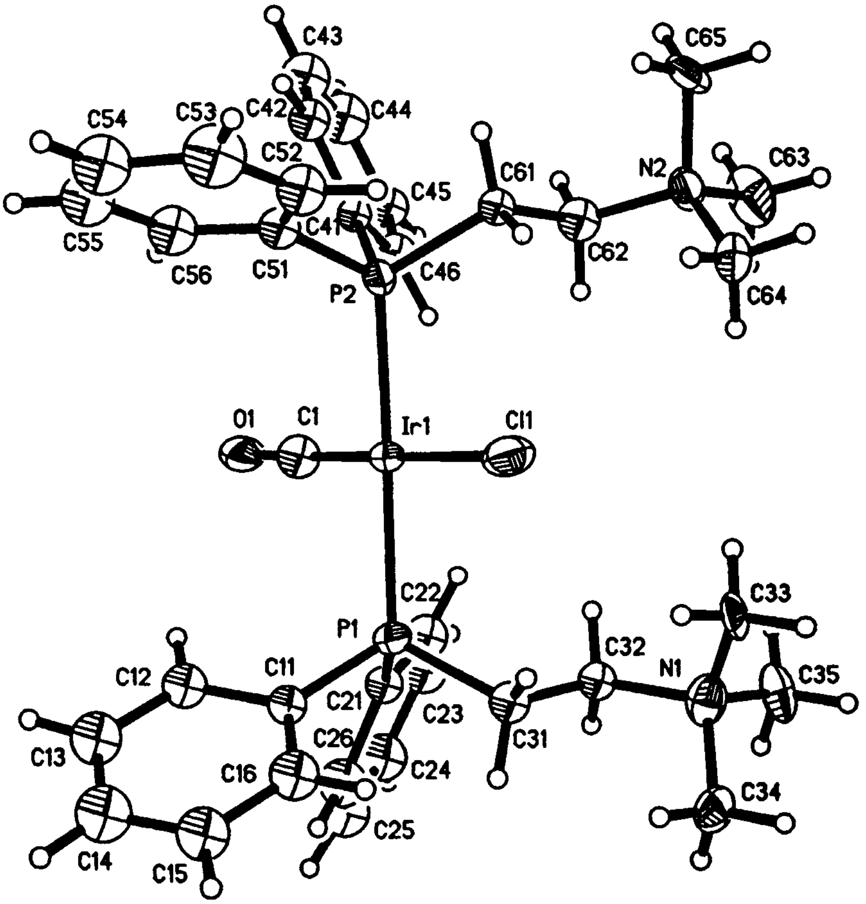


FIGURE 4 Geometry of the [*trans*-Ir(CO)Cl(PPh$_2$CH$_2$CH$_2$NMe$_3$)$_2^{2+}$] cation.

HCl (reaction with H_2) and cation formation (reaction with CO) that are related to the polar solvents used.

Supplementary Data

Tables of atomic coordinates, bondlengths, bond angles, anisotropic thermal parameters and calculated positions for the hydrogen atoms for the two structural studies (11 pages) are available from the authors.

Acknowledgments

J.D.A. is grateful to the Department of Energy, ER13775 for support of this research. Purchase of the diffractometer was made possible by Grant

Downloaded At: 15:07 23 January 2011

89-13733 from the Chemical Instrumentation Program of the National Science Foundation.

References

[1] (a) D.M. Roundhill, *Adv. Organomet. Chem.*, **38**, 155 (1995). (b) M. Beller, B. Cormile, C.D. Frohning, C.W. Kohlpaintner, *J. Mol. Cat. A*, **104**, 17 (1995). (c) W. Herrmann, C.W. Kohlpaintner, *Angew. Chem. Int. Ed. Engl.*, **32**, 1524 (1993). (d) P. Kalck, F. Monteil, *Adv. Organomet. Chem.*, **34**, 219 (1992). (e) M. Barton, J.D. Atwood, *J. Coord. Chem.*, **24**, 43 (1991) (f) F. Joó, Z. Toth, *J. Mol. Cat.*, **8**, 369 (1980).

[2] (a) R.T. Smith, M.C. Baird, *Trans. Met. Chem.*, **6**, 197 (1981). (b) R.T. Smith, M.C. Baird, *Inorg. Chim. Acta* **62**, 135 (1982). (c) M. K. Markiewicz, M. C. Baird, *Inorg. Chim. Acta*, **113**, 95 (1986).

[3] E. Renaud, R.B. Russell, S. Fortier, S.J. Brown, M.C. Baird, *J. Organomet. Chem.*, **419**, 403 (1991).

[4] (a) C.T. Sears, M. Kubota, *Inorg. Synth.*, **11**, 1101 (1968). (b) H.J. Lawson, J.D. Atwood, *J. Am. Chem. Soc.*, **111**, 6223 (1989).

[5] G. Wilkinson, *Inorg. Synth.*, **13**, 127 (1972).

[6] M.R. Churchill, R.A. Lashewycz, F.J. Rotella, *Inorg. Chem.*, **16**, 265 (1977).

[7] G.M. Sheldrick, *SHELXTL PLUS, Release 4.11* (*VMS*); Siemens Analytical Instruments Inc.: Madison, WI (1989).

[8] G.M. Sheldrick, *SHELXTL PLUS, An integrated system for solving, refining and displaying crystal structures from diffraction data; For Nicolet R3m/V*; University of Göttingen, Germany (1987).

[9] *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, (1974), Vol. 4, Table 2.2B, pp. 99–101.

[10] Ref. 7, Table 2.3.1, pp. 149–150.

[11] M.R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973).

[12] D. Rogers, *Acta Crystallogr. Series A*, **A37**, 734 (1981).

[13] T. Ueki, A. Zalkin, D.H. Templeton, *Acta Crystallogr.*, **20**, 836 (1966).

[14] J.F. Harrod, W.J. Yorke, *Inorg. Chem.*, **20**, 1156 (1981).

[15] M.J. Burke, M.P. McGrath, R. Wheeler, R.H. Crabtree, *J. Am. Chem. Soc.*, **110**, 5034 (1988).

[16] (a) D.P. Paterniti, P.J. Roman Jr., J.D. Atwood, submitted. (b) D.P. Paterniti, P.J. Roman Jr., J.D. Atwood, *J. Chem. Soc., Chem. Commun.*, 2659 (1996).

[17] M.R. Churchill, J.C. Fettinger, B.J. Rappoli, J.D. Atwood, *Acta Crystallogr., Series C*, **C43**, 1697 (1987).

[18] M.R. Churchill, J.C. Fettinger, L.A. Buttrey, M.D. Barkan, J.S. Thompson, *J. Organomet. Chem.*, **340**, 257 (1988).

[19] M.R. Churchill, S. A. Julis, *Inorg. Chem.*, **17**, 3011 (1978).

Downloaded At: 15:07 23 January 2011