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*Aust. J. Chem.* **2017**, *70*, 1180–1187
https://doi.org/10.1071/CH17173

Full Paper

# Reactions of Trivalent Iodine Reagents with Classic Iridium and Rhodium Complexes*

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In this work, the reactions of iodine(III) reagents ($PhI(L)_2$: L = pyridine, acetate ($OAc^-$), triflate ($OTf^-$)) with iridium(I) and rhodium(I) complexes (Vaskas's compound, Wilkinson's catalyst, and bis[bis(diphenylphosphino)ethane]rhodium(I) triflate) are reported. In all cases, the reactions resulted in two-electron oxidation of the metal complexes. Mixtures of products were observed in the reactions of $I^{III}$ reagents with Vaska's compound and Wilkinson's catalyst via ligand exchange and anion scrambling. In the case of reacting $I^{III}$ reagents with chelating ligand-containing bis[bis(diphenylphosphino)ethane]rhodium(I) triflate, no scrambling was observed.

Manuscript received: 27 March 2017.
Manuscript accepted: 7 July 2017.
Published online: 9 August 2017.

## Introduction

Iodine(III) reagents with a $PhI(L)_2$ motif (L = −Cl, −OAc, pyridine) have attracted much attention as stoichiometric oxidants owing to their ease of handling, low toxicity, and ability to act as oxidizing reagents under mild conditions.[1] They have become a popular way to interrogate higher-oxidation-state late transition metal complexes.[2] For example, these reagents have been successfully used in isolating or accessing higher oxidation states of platinum group metals.[3–10] The Sanford group has demonstrated the use of these iodine reagents in investigating C–H bond activation at $Pd^{IV}$ centres. The oxidation of compound **1** by either $PhICl_2$ or $PhI(OAc)_2$ resulted in the isolation and characterization of rare $Pd^{IV}$ organometallic complexes **1Cl** and **1OAc** (Scheme 1). At elevated temperatures, these compounds undergo reductive elimination, with C–C, C–Cl, and C–O bond-forming reactions.[3,11]

Our group have been using dicationic $I^{III}$ reagents $[PhI(L)_2][OTf]_2$ (L = pyridine, 4-dimethylaminopyridine) to explore the chemistry of the II–IV redox couple for Pd and Pt and the I–III couple for Au (Schemes 2, 3).[6,12] These reagents were first synthesized by Weiss in 1994 and later investigated by Zhdankin.[13,14] These dicationic $I^{III}$ reagents typically simultaneously oxidize the transition metal and deliver the neutral ligands, allowing the isolation of charged metal complexes. The oxidation of compound **1** by $[PhI(L)_2][OTf]_2$ (**2R**) resulted in an unexpected outcome, as shown in Scheme 2. The reaction is proposed to proceed through oxidation of $Pd^{II}$ to give an unobserved $Pd^{IV}$ intermediate, which undergoes reductive elimination, resulting in C–C bond formation by linking two 2-phenylpyridine ligands. Ligand redistribution then gives the observed products **3** and **4**.[6]

Our group also reported a new class of tri-cationic gold(III) complexes using the dicationic $I^{III}$ reagents, as shown in Scheme 3,[12] where the reaction of compound **1** with **2R** resulted in simultaneously oxidizing $Au^{I}$ to $Au^{III}$ and delivering pyridine ligands to form compound **6**.

Ritter has reported the use of the dicationic $I^{III}$ reagent **2CN** in the isolation of a $Pd^{IV}$ complex (Scheme 4). The oxidation of compound **7** using **2CN** resulted in the formation of $Pd^{IV}$ with a single ligand transfer to give compound **8**. This complex was then used in the formation of a late-stage fluorinating agent via displacement of pyridine with $^{18}F^-$ to generate complexes that have potential to be used in positron emission tomography (PET) imaging.[15]

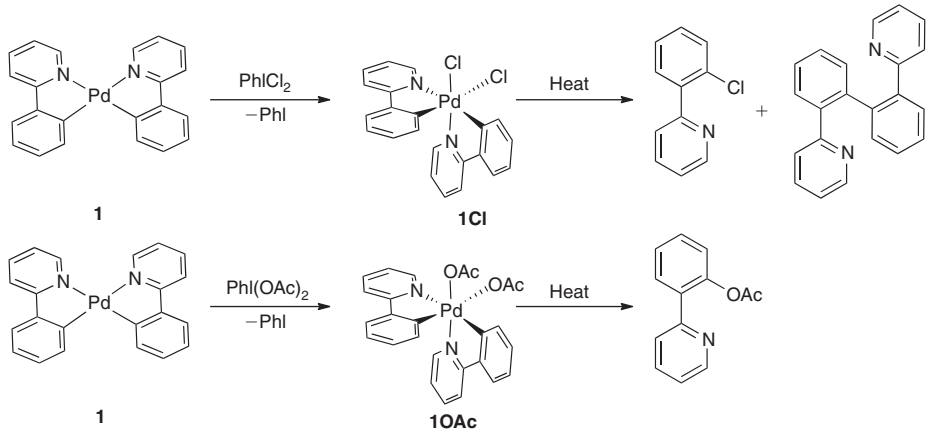
Our group has been specifically avoiding phosphine-containing metal complexes in this chemistry because it was observed that phosphine ligands react with $I^{III}$ reagents, resulting in oxidation of the phosphine.[16] In the present study, we explored the reactions of selected phosphine-containing $Ir^{I}$ and $Rh^{I}$ complexes with $I^{III}$ reagents containing anionic and neutral ligands (Fig. 1) and examined if the iodine(III) reagents would be compatible with these phosphine-containing iridium and rhodium complexes. A very recent review on the area indicated very little work has been done examining the reactions of iridium and rhodium complexes with $I^{III}$.[17]

## Experimental

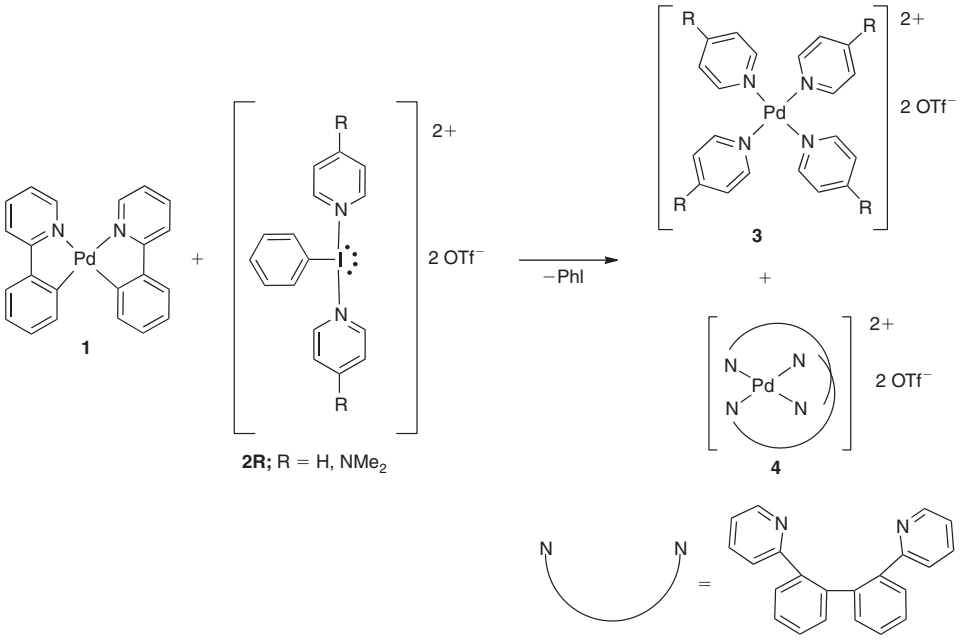
### *Materials and Methods*

NMR solvents were purchased from Cambridge Isotope Laboratories and dried by stirring for 3 days over $CaH_2$, which was distilled and stored over 3-Å molecular sieves in a glovebox. $CH_2Cl_2$, $CH_3CN$, *n*-hexane, toluene, and chloroform, which were purchased from Caledon Laboratories, were dried using an Innovative Technologies solvent purification system. All solvents were

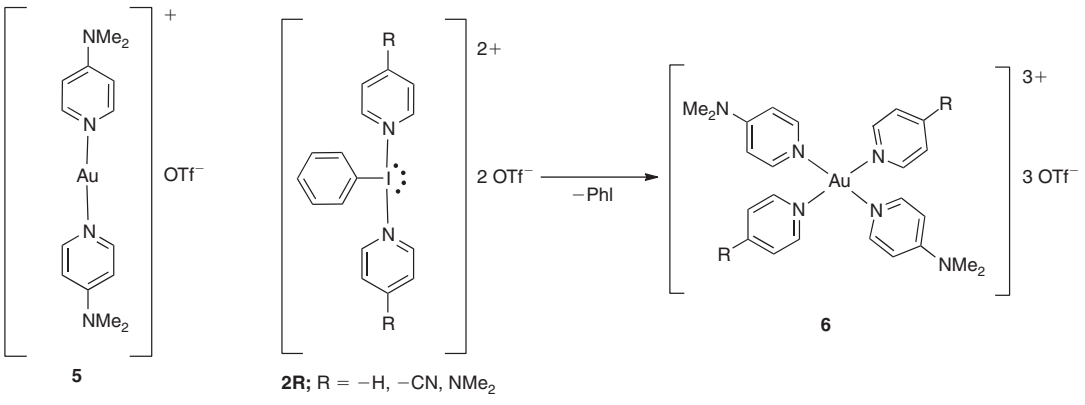
*Jason Dutton is the recipient of the 2016 Alan Sargeson Lectureship.



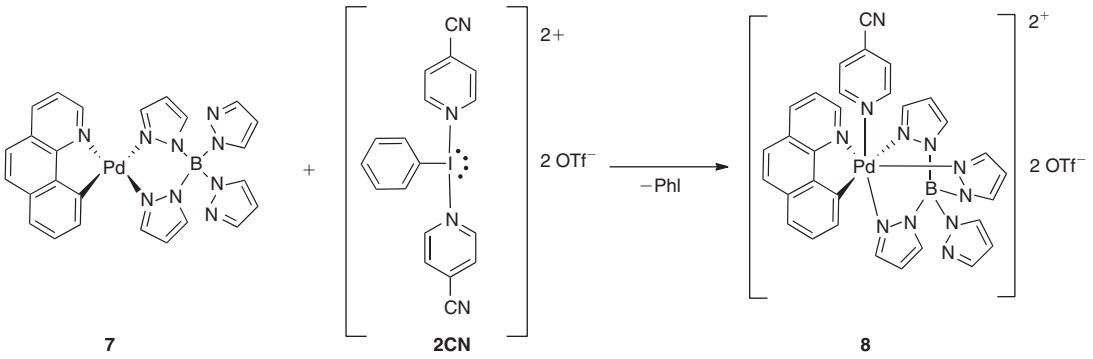

**Scheme 1.** Oxidation of compound **1** using $PhICl_2$ and $PhI(OAc)_2$.




**Scheme 2.** Reaction of compound **1** with dicationic $I^{III}$ reagents.




**Scheme 3.** Synthesis of $Au^{III}$ complex **6**.




**Scheme 4.** Reaction of dicationic $I^{III}$ reagent with $Pd^{II}$.

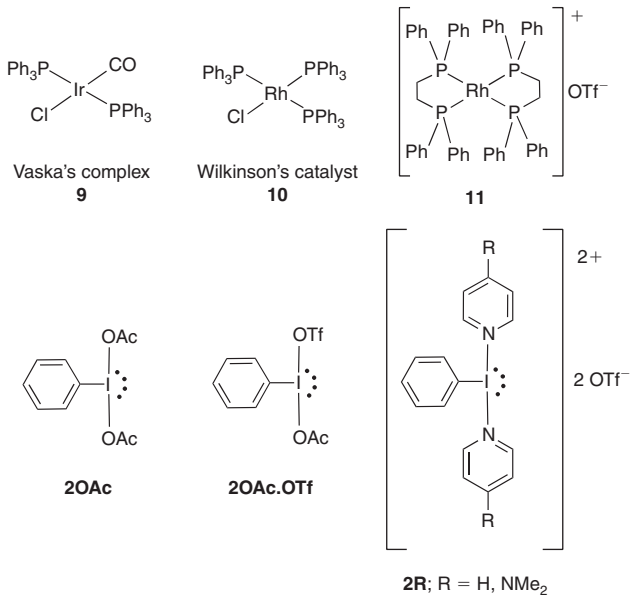



**Fig. 1.** Iridium(I), rhodium(I), and iodine(III) reagents used in the present study.

stored over 3-Å molecular sieves in a nitrogen-filled glovebox. All remaining reagents were ordered from Sigma–Aldrich and used as received. $Ir(PPh_3)_2(CO)Cl$,[18] $Rh(PPh_3)_3Cl$,[19] $[Rh(dppe)_2][Cl]$ (dppe = bis(diphenyl)phosphinoethane),[20] $[PhI(Pyr)_2][OTf]_2$ (pyr = pyridine), and $[PhI(4\text{-}DMAP)_2][OTf]_2$ (DMAP = 4-dimethylaminopyridine)[13] were prepared following published procedures. The metathesis to produce $[Rh(dppe)_2][OTf]$ was carried out by the addition of a 1 : 1 stochiometric ratio of TMS-OTf (OTf = triflate) to a $CH_2Cl_2$ solution of $[Rh(dppe)_2][Cl]$ followed by solvent removal at reduced pressure.

CCDC numbers 1539214–1539218 at the Cambridge Crystallographic Data Centre contain the crystallographic data for this manuscript in .cif format.

### *Reaction of **2OAc** with **9***

A solution of **2OAc** (42 mg, 0.13 mmol) in 2 mL $CDCl_3$ was added dropwise to a solution of **9** (100 mg, 0.13 mmol) in 5 mL $CDCl_3$ and stirred for 3 h at room temperature. A colour change from bright yellow to light yellow was observed within 10 min. The solvent was reduced to half under reduced pressure, followed by addition of 10 mL *n*-hexane, which resulted in precipitation of a pale yellow solid. The solid was filtered, washed with *n*-hexane (2 × 10 mL), and dried under reduced pressure. $\delta_P$ (162 MHz, $CDCl_3$) 2.0 (s), −1.6 (s), −9.6 (s), −10.9 (s), −12.6, −13.7 (s). See the Supplementary Material for the $^1H$ NMR. *m*/*z* (electrospray ionization mass spectrometry (ESI-MS)) ($[M]^{n+}$) 876.1 $[Ir(PPh_3)_2(CO)(Cl)_2(OAc)]$, 894.1 $[Ir(PPh_3)_2(OAc)_3]$.

### *Reaction of **2R** with **9***

A solution of **2R** (0.13 mmol) in 5 mL $CDCl_3$ was added dropwise to a solution of **9** (100 mg, 0.13 mmol) in 5 mL $CDCl_3$ and stirred for 3 h at room temperature. A colour change from bright yellow to light yellow was observed within 30 min. The solvent was reduced to half under reduced pressure, followed by addition of 10 mL *n*-hexane, which resulted in precipitation of a pale yellow solid. The solid was filtered, washed with *n*-hexane (2 × 10 mL), and dried under reduced pressure. R = **$NMe_2$**: $\delta_P$ (162 MHz, $CDCl_3$) −2.4 (s), −8.4 (s), −15.4 (s). See the Supplementary Material for the $^1H$ NMR. *m*/*z* (ESI-MS) $([M]^{n+})^+$ 797.1 $[Ir(PPh_3)(CO)(Cl)_2(DMAP)_2]^+$, 937.0 $[Ir(PPh_3)_2(CO)(Cl)_2(DMAP)]^+$. R = **H**: $\delta_P$ (162 MHz, $CDCl_3$) 65.9 (s), 26.9 (s), −3.9 (s), −14.6 (s), −15.2 (s), −16.4 (s), −23.1 (s). *m*/*z* (ESI-MS) ($[M]^{n+}$) 711.1 $[Ir(PPh_3)(CO)(Cl)_2(Pyr)_2]^+$, 894.1 $[Ir(PPh_3)_2(CO)(Cl)_2(Pyr)]^+$.

### *Reaction of **2OAc.OTf** with **9***

A mixture of **2OAc** (20 mg, 0.064 mmol) and TMS-OTf (23 μL, 0.128 mmol) in 2 mL $CDCl_3$ was added dropwise to a solution of **9** (50 mg, 0.064 mmol) in 2 mL $CDCl_3$. A colour change from bright yellow to brown was observed in 10 min. An aliquot was removed for NMR and mass spectrometry analysis. $\delta_P$ (162 MHz, $CDCl_3$) 14.4 (s), 8.0 (s), 5.3 (s), 2.6 (s), 0.4 (s), −3.6 (s), −8.1 (s), −15.6 (s), −21.4 (s). *m*/*z* (ESI-MS) ($[M]^{n+}$) 745.2 $[Ir(PPh_3)_2CO]^+$, 753.2 $[Ir(PPh_3)_2Cl]^+$, 786.1 $[Ir(PPh_3)_2Cl_2]^+$, 803.1 $[Ir(PPh_3)_2CO(OAc)]^+$, 839.1 $[Ir(PPh_3)_2CO(OAc)Cl]^+$.

### *Reaction of **2OAc** with **10***

A solution of **2OAc** (35 mg, 0.11 mmol) in 2 mL $CDCl_3$ was added dropwise to a solution of **10** (100 mg, 0.11 mmol) in 5 mL $CDCl_3$ and stirred for 3 h at room temperature. A colour change from burgundy to light red was observed. The solvent was reduced to half under reduced pressure, followed by addition of 10 mL *n*-hexane, which resulted in precipitation of a light orange solid. The solid was filtered, washed with *n*-hexane (2 × 10 mL), and dried under reduced pressure. $\delta_P$ (162 MHz, $CDCl_3$) 24.5 (d, *J* 122). $\delta_H$ (400 MHz, $CDCl_3$) 7.43–7.38 (m, 6H), 7.37–7.32 (m, 12H), 7.20–7.17 (m, 12H), 2.08 (s, 3H). $\delta_C$

(100 MHz, $CDCl_3$) 191.24, 135.61, 130.94, 129.28, 127.71, 25.70. *m/z* (ESI-MS) ($[M]^{n+}$) 721.1 $[Rh(PPh_3)_2(Cl)(OAc)]^+$.

### *Reaction of **2R** with **10***

A solution of **2R** (0.11 mmol) in 5 mL $CDCl_3$ was added dropwise to a solution of **10** (100 mg, 0.11 mmol) in 5 mL $CDCl_3$ and stirred for 3 h at room temperature. A colour change from burgundy to light red-brown was observed. The solvent was reduced to half under reduced pressure, followed by addition of 10 mL *n*-hexane, which resulted in precipitation of a light brown solid. The solid was filtered, washed with *n*-hexane (2 × 10 mL), and dried under reduced pressure. R = **$NMe_2$**: $\delta_P$ (162 MHz, $CH_2Cl_2$) 28.2 (s), 14.1 (d, *J* 88), 11.9 (d, *J* 88). *m/z* (ESI-MS) ($[M]^{n+}$) 803.0 $[Rh(PPh_3)(Cl)_2(DMAP)_3]^+$, 942.2 $[Rh(PPh_3)_2(Cl)_2(DMAP)_2]^+$. R = **H**: $\delta_P$ (162 MHz, $CH_2Cl_2$) 65.0 (s), 14.0 (d, *J* 84), 9.7 (d, *J* 104). *m/z* (ESI-MS) ($[M]^{n+}$) 673.6 $[Rh(PPh_3)(Cl)_2(Pyr)_3]^+$, 854.9 $[Rh(PPh_3)_2(Cl)_2(Pyr)_2]^+$.

### *Reaction of **2OAc.OTf** with **10***

A mixture of **2OAc** (17 mg, 0.054 mmol) and TMS-OTf (20 µL, 0.108 mmol) in 2 mL $CDCl_3$ was added dropwise to a solution of **10** (50 mg, 0.054 mmol) in 2 mL $CDCl_3$. A colour change from burgundy to brown was observed in 10 min. An aliquot was removed for NMR and mass spectrometry analysis. $\delta_P$ (162 MHz, $CDCl_3$) 61.9 (s), 45.2 (dt, *J* 135), 23.4 (s), 19.8 (dt, *J* 100). *m/z* (ESI-MS) ($[M]^{n+}$) 297.1 $[PPh_3Cl]^+$, 307.1 $[RhIPh]^+$, 406.0 $[RhPPh_3NCCH_3]^+$, 477.0 $[RhPPh_3Cl_2NCCH_3]^+$, 568.9 $[PPh_3RhIPh]^+$, 627.0 $[Rh(PPh_3)_2]^+$, 697.0 $[Rh(PPh_3)_2Cl_2]^+$.

### *Reaction of **2OAc** with **11***

A mixture of **2OAc** (31 mg, 0.095 mmol) and TMS-OTf (35 µL, 0.19 mmol) in 5 mL $CH_2Cl_2$ was added dropwise to a solution of **11** (100 mg, 0.095 mmol) in 5 mL $CH_2Cl_2$ and stirred for 1 h at room temperature. A colour change from bright yellow to yellow was observed within 5 min. The solvent was reduced to half under reduced pressure, followed by addition of 10 mL *n*-hexane, which resulted in precipitation of a yellow solid. The solid was filtered, washed with *n*-hexane (2 × 10 mL), and dried under reduced pressure (84 mg, 70 % yield). $\delta_P$ (162 MHz, $CH_2Cl_2$) 58.6 (dt, *J* 11, 84), 42.5 (dt, *J* 11, 115). $\delta_H$ (400 MHz, $CD_3CN$) 7.81–7.76 (m, 8H), 7.68–7.60 (m, 8H), 7.58–7.56 (m, 12H), 7.39–7.34 (m, 4H), 7.24–7.20 (m, 4H), 7.18–7.15 (m, 4H), 2.68–2.56 (m, 8H), 1.96 (s, 3H). $\delta_C$ (100 MHz, $CD_3CN$) 172.07, 134.55, 134.08, 133.55, 133.25, 130.45, 130.24, 126.05, 125.51, 24.37, 20.22, 16.68. *m/z* (ESI-MS) ($[M]^{n+}$) 479.1 $[Rh(dppe)_2(OAc)]^{2+}$.

### *Reaction of **2NMe$_2$** with **11***

A solution of **2$NMe_2$** (72 mg, 0.095 mmol) in 5 mL $CDCl_3$ was added dropwise to a solution of **11** (100 mg, 0.095 mmol) in 5 mL $CDCl_3$ and stirred for 3 h at room temperature. A colour change from bright yellow to yellow was observed. The solvent was reduced to half under reduced pressure, followed by addition of 10 mL *n*-hexane, which resulted in precipitation of a pale orange solid. The solid was filtered, washed with *n*-hexane (2 × 10 mL), and dried under reduced pressure (80 mg, 53 % crude yield). $\delta_P$ (162 MHz, $CDCl_3$) 30.8 (s), 40.7 (dt, *J* 15, 113), 34.5 (dt, 15, 86). $\delta_H$ (400 MHz, $CDCl_3$) 7.98–6.65 (m, 50H), 3.19 (s, 12H). *m/z* (ESI-MS) ($[M]^{n+}$) 380.7 $[Rh(dppe)_2(DMAP)_2]^{3+}$, 510.1 $[Rh(dppe)_2(DMAP)]^{2+}$.

## Results and Discussion

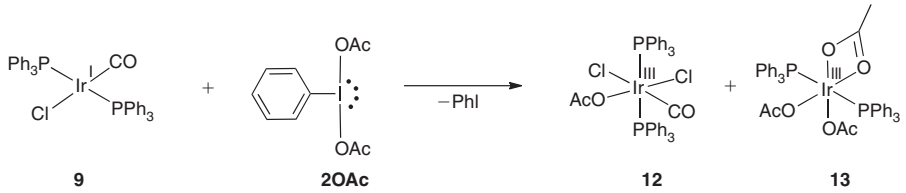
Treatment of **9** with **2OAc** in $CDCl_3$ for 3 h resulted in a pale yellow solution. The $^{31}P$ NMR spectrum of the reaction mixture gave six peaks between 2.0 and −13.7 ppm, indicating the presence of a mixture of products. Oxidation of the phosphine ligands as inferred from no strongly downfield-shifted signals was, however, not observed. The cationic ESI mass spectrum of the reaction mixture indicated the presence of compounds **12** and **13** at *m/z* 876.1 and 894.1 (Scheme 5). X-Ray diffraction studies were done on two single crystals of different morphologies obtained from vapour diffusion of $Et_2O$ into a concentrated $CH_2Cl_2$ solution of the mixture, which showed the crystals to be $Ir^{III}$ compounds **12** and **13** (Fig. 2). The bond distances and geometries of the complexes are all typical and therefore do not warrant any further discussion. The similar solubility of these products prevented their separation from each other. Compound **12** gained one chloride and one acetate whereas compound **13** lost a chloride and a CO, and gained three acetates. It is obvious that using $I^{III}$ oxidant with **9** resulted in a mixture of products, possibly arising from ligand exchange and anion scrambling. It has been reported that the use of $I^{III}$ oxidant in other systems such as $Au^I/Au^{III}$ resulted in significant ligand and anion scrambling.[12,21,22]

The reaction of **9** with **2OAc.OTf** in a 1 : 1 ratio resulted in a colour change from bright yellow to brown within 10 min. The $^{31}P$ NMR of the reaction mixture contained seven peaks between −22 and 15 ppm, indicating the presence of seven phosphorus-containing products. The positive ESI detection mass spectrum showed a similar scrambling pattern to that found from **2OAc** with **9**, with compound **12** being present.

Treatment of **9** with **2$NMe_2$** in $CDCl_3$ at room temperature for 3 h resulted in a colour change from bright yellow to light yellow. The $^{31}P$ NMR spectrum of the isolated solid in $CDCl_3$ gave three peaks at −2.4, −8.4, and −15.4 ppm indicating the presence of three phosphorus-containing products. Positive mode ESI-MS detection of a $CH_3CN$ solution of the isolated solid gave fragments that could be identified at $[m/z]^+ = 797.1$ consistent with **14$NMe_2$** and $[m/z]^+ = 937.1$ consistent with **15$NMe_2$** as shown in Scheme 6. The stereochemistry of **14$NMe_2$** cannot be determined from the data. The presence of one unique P environment in **15$NMe_2$** inferred by the lack of P–P coupling allows the assignment of $PPh_3$ ligands as *trans* to one another, but the configuration of the other ligands relative to each other cannot be determined.

X-Ray diffraction studies were done on single crystals obtained from vapour diffusion of $Et_2O$ into concentrated $CH_2Cl_2$ solution of the isolated solid, which revealed compound **16.** This compound has been synthesized previously by reacting $IrCl(PPh_3)_3$ with chlorine.[23] The use of the $I^{III}$ oxidant **2H** resulted in a similar outcome, where the ESI-MS spectrum contained fragments consistent with **14R** and **15R**. The $^{31}P$ NMR spectrum of the isolated solid contained signals between 65.9 and −23.1 ppm. The signal at 65.9 ppm is consistent with the formation of the chlorophosphonium cation ($[Ph_3PCl]^+$),[24] which may occur via reductive elimination from $Ir^{III}$. Overall, the reaction of Vaska's complex **9** with the chosen $I^{III}$ oxidants resulted in significant ligand and anion scrambling.

The reaction of **10** with **2OAc** in $CDCl_3$ at room temperature for 3 h resulted in a colour change to light reddish-brown. The $^{31}P$ NMR spectrum of the reaction mixture contained two doublets at 24.5 and 28.3 ppm. The two doublets were taken to represent two chemically distinct phosphorus atoms coupling




**Scheme 5.** Reaction of **9** with **2OAc** products as identified by mass spectrometry and X-ray crystallography.

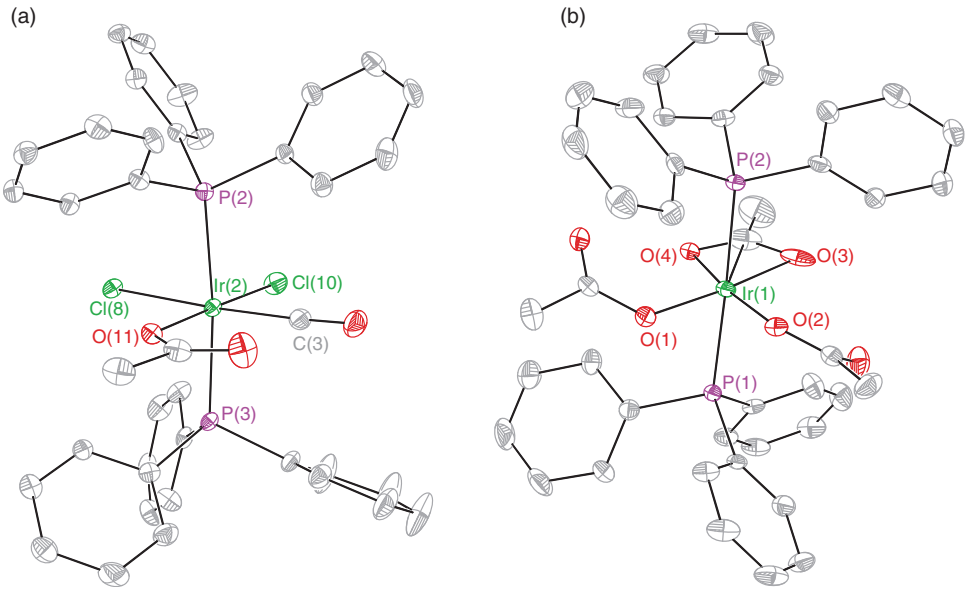
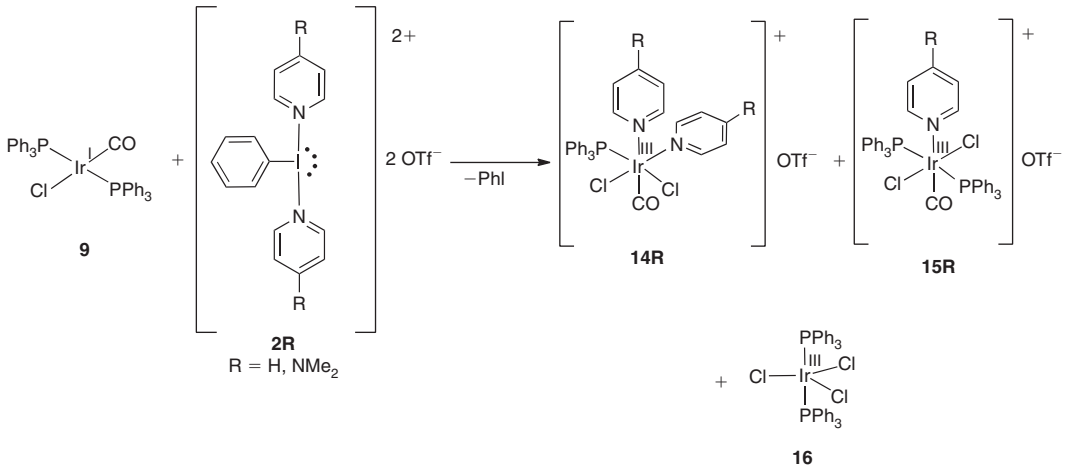



**Fig. 2.** (a) Solid-state structure of **12**. Ellipsoids are depicted at the 50 % probability level, and hydrogen atoms have been removed for clarity. (b) Solid-state structure of **13**. Ellipsoids are depicted at the 50 % probability level, and hydrogen atoms have been removed for clarity.




**Scheme 6.** Reaction of **9** with **2R** products as identified by mass spectrometry and X-ray crystallography.

with $^{103}$Rh, which suggests the presence of two compounds, each with one unique $^{31}$P environment.

The most abundant signal in the mass spectrum ($[m/z]^+$ 721.1) resulted from loss of one chloride from compound **17.** A cationic fragment at $[m/z]^+ = 745.1$ could result from the loss of one acetate from proposed compound **18**. Compound **17** was isolated by dissolving the solid in a minimum amount of $CH_2Cl_2$ and placing at −35°C overnight. The solid then was filtered and washed with *n*-hexane. X-Ray diffraction studies performed on single crystals obtained from concentrated $CH_2Cl_2$ solution of the isolated solid at −35°C confirmed product **17** as shown in Fig. 3. The bond distances and geometry are all typical and therefore do not warrant further discussion. The reaction is proposed to proceed via oxidation of **10** to give an unobserved intermediate, which is followed by ligand redistribution and anion scrambling to give the observed products as shown in Scheme 7.

The dropwise addition of **2NMe$_2$** to **10** at room temperature in $CDCl_3$ resulted in a colour change from burgundy to light red over 3 h. The $^{31}$P NMR spectrum of the reaction mixture had two doublets at 14.1 and 11.9 ppm, indicating two phosphorus-containing products coupling to Rh in the mixture. A singlet at 28.2 ppm could not be identified. The positive ESI-MS detection of the mixture indicated the presence of **19** and **20** at $[m/z]^+ = 942.2$ and 803.0, which also was consistent with the chlorine isotope patterns, as shown in Scheme 8. The similar solubilities of these products prevented their isolation. Using I$^{III}$ oxidant **2H** resulted in similar Rh products as indicated by mass spectrometry and $^{31}$P NMR spectroscopy. As with the reaction of **9** with **2H**, the $^{31}$P NMR also contained a singlet at 65.0 ppm, indicating the presence of the chlorophosphonium cation $[Ph_3PCl]^+$. The presence of doublets rather than doublets of doublets indicates the P atom environments are identical within each of the two compounds; therefore, the stereochemistry is proposed to be as depicted for **19R** in Scheme 8, although for **20R**, this cannot be ascertained.

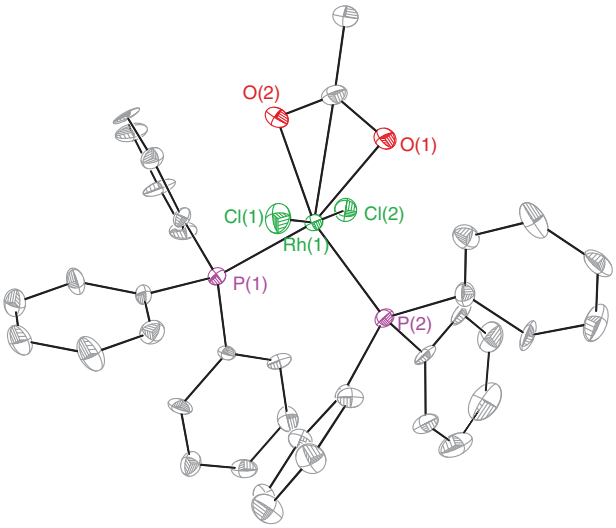
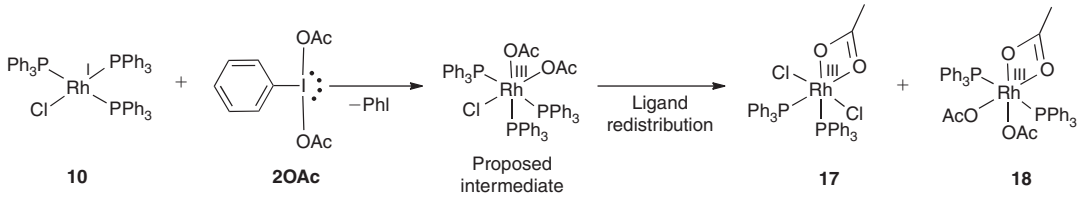
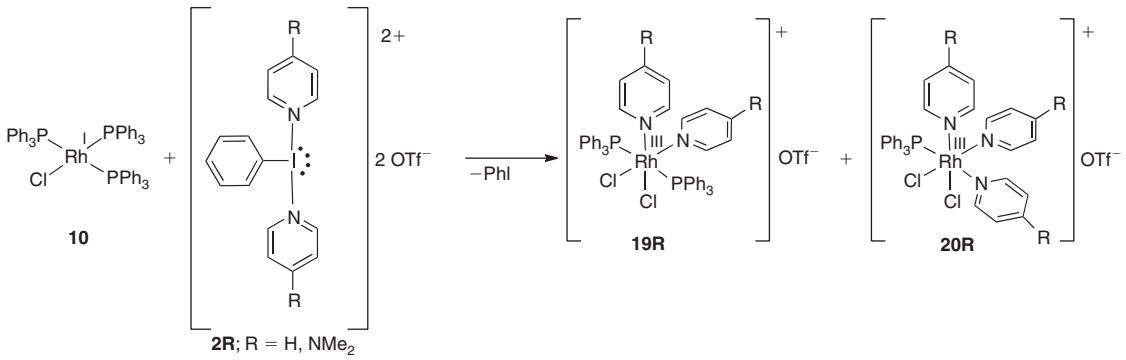



**Fig. 3.** Solid-state structure of **17**. Hydrogen atoms omitted for clarity. Thermal ellipsoids shown at the 50 % probability level.

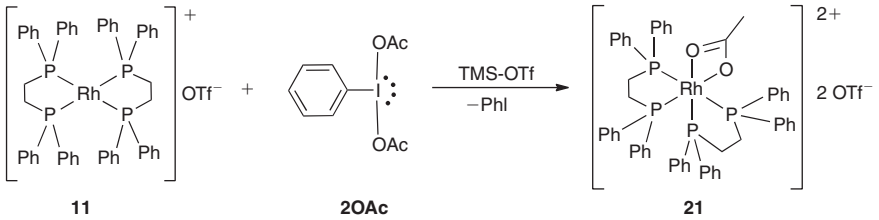
The slow addition of **2OAc.OTf** to **10** in 1 : 1 ratio resulted in a colour change from burgundy to brown within 10 min. The $^{31}$P NMR of the reaction mixture had four signals between 4 and 62 ppm. The major singlet at 62 ppm represents the chlorophosphonium cation $[Ph_3PCl]^+$, which was also observed in the mass spectrum of the reaction mixture at *m/z* 297.1. The two doublets at 45.2 ($J_{P-Rh} = 135$ Hz) and 19.8 ppm ($J_{P-Rh} = 100$ Hz) represent two P–Rh containing products. The cationic ESI mass spectrum of the reaction mixture contained fragments at $m/z =$ 568.9 and 697.1, which were assigned to $[Rh(PPh_3)(Ph)]^+$ and $[Rh(PPh_3)_2(Cl)_2]^+$ respectively. The former product indicates that it is possible for the I–Ph fragment of the iodine(III) oxidant to




**Scheme 7.** Reaction of **10** with **2OAc** products as identified by mass spectrometry and X-ray crystallography.




**Scheme 8.** Reaction of **10** with **2R** products as identified by mass spectrometry.




**Scheme 9.** Reaction of **11** with **2OAc.OTf** product as identified by mass spectrometry and X-ray crystallography.

also become involved in these reactions, which has also been observed in related chemistry with thiophenes, selenophenes, and tellurophenes using this family of oxidants.[25–27]

As with Vaska's complex, the overall result using $PhIL_2$ $I^{III}$ oxidants with Wilkinson's catalyst resulted in significant scrambling and overall unproductive reactions.

Treatment of homoleptic bis-dppe chelated $Rh^{I}$ compound **11** with **2OAc** in $CDCl_3$ at room temperature for 3 h resulted in no colour change. The $^{31}P$ NMR spectrum of the reaction mixture also indicated no reaction had taken place, showing only starting material. The oxidation of this compound required the use of the stronger oxidizing reagent **2OAc.OTf** reagent, prepared by the addition of 2 equivalents of TMS-OTf to **2OAc** to give **2OAc.OTf** (leaving a free equivalent of TMS-OTf).[16,28,29] The dropwise addition of a $CH_2Cl_2$ solution containing PhI(OAc)(OTf) and TMS-OTf to compound **11** resulted in a colour change from bright yellow to yellow and gave a yellow solid after a short workup. The positive ESI-MS spectrum of the isolated solid redissolved in $CH_3CN$ showed a major peak at $[m/z]^+ = 479.1$ with a half-mass-unit peak separation that is consistent with **21** as shown in Scheme 9. Further characterization of compound **21** by X-ray crystallography confirmed that this complex contained one acetate group bound to the dicationic $Rh^{III}$ in a bidentate fashion as shown in Fig. 4, with the two dppe ligands retained.

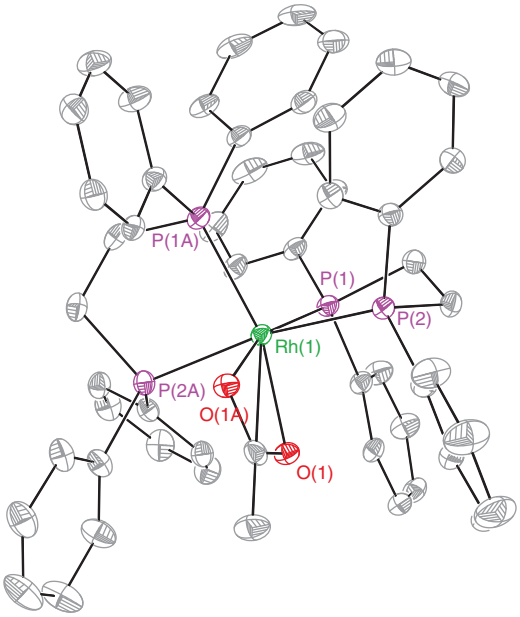


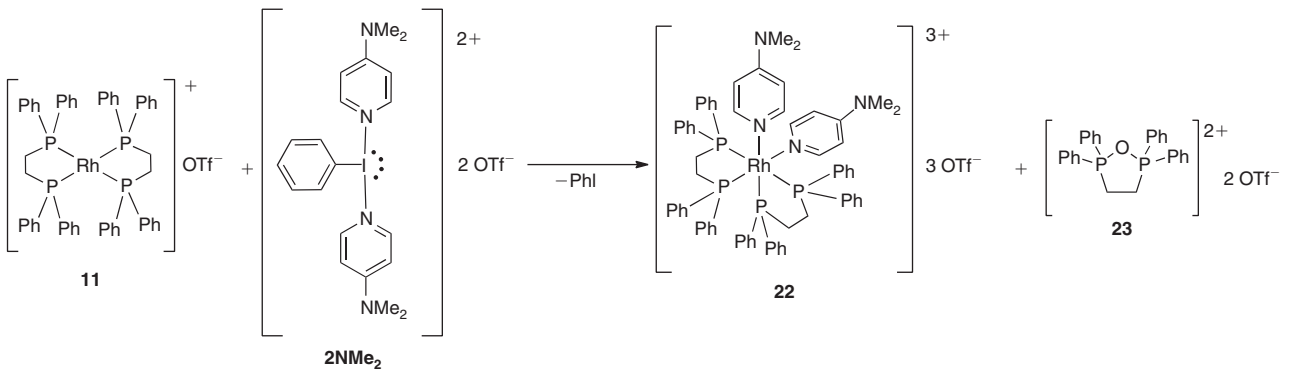

**Fig. 4.** Solid-state structure of **21**. Hydrogen atoms and triflate counter ions omitted for clarity. Thermal ellipsoids shown at the 50 % probability level.

Treatment of compound **11** with **2NMe** in $CDCl_3$ at room temperature for 3 h followed by workup resulted in the isolation of a yellow solid. The $^{31}P$ NMR spectrum of the isolated solid showed two doublets of triplets at 40.7 and 34.5 ppm, which is consistent with proposed product **22**, as well as a singlet at 30.8 ppm. Searching the literature revealed that 1,2-bis(diphenylphosphinyl)ethane (**23**) has been reported to give an identical chemical shift to our observation (30.8 ppm).[30] The positive ESI-MS analysis of the isolated solid shows a major peak at $[m/z]^+ = 510.1$ with a half-mass-unit peak separation and a minor peak at $[m/z]^+ = 380.7$ with one-third mass-unit peak separation, which is in agreement with compound **22** as shown in Scheme 10.

Compound **23** and related phosphine oxide species have been observed to be generated from high-oxidation-state phosphorus triflate species.[16,31] Compounds **22** and **23** were shown to be in approximate ratio of 4 : 1 by $^{31}P$ NMR, bearing in mind the semiquantitative nature of $^{31}P$ NMR. A battery of efforts to selectively precipitate **22** to obtain an analytically pure sample unfortunately failed.

## Conclusion

Reactions of trivalent iodine reagents containing a $PhI(L)_2$ motif with classic iridium and rhodium complexes have been reported. The metal complexes under study were successfully oxidized from +1 to +3. Oxidations of Vaska's compound generally resulted in a mixture of products via ligand exchange and anion scrambling. In the case of Wilkinson's catalyst, the oxidation also resulted in a mixture of products due to ligand exchange and anion scrambling. Reactions of trivalent iodine reagents with homoleptic $Rh^{I}$ bound by chelating phosphines (compound **11**) resulted in cleaner oxidation of $Rh^{I}$ to $Rh^{III}$ and suggests that these systems have a better compatibility with $I^{III}$ reagents. In most cases, oxidized phosphine was not observed, likely resulting from reductive elimination from the high-oxidation-state metal complexes rather than direct oxidation of the phosphines, indicating $I^{III}$ is reasonably compatible with metal-bound phosphine-containing complexes. However, ligand scrambling in the oxidized species can clearly present a major problem in terms of accurately predicting reaction outcomes and isolating clean products in good yields.




**Scheme 10.** Products of the reaction of **11** with **2NMe$_2$** as identified by mass spectrometry.

## Supplementary Material

Experimental details, $^{1}H$, $^{31}P$ NMR spectra, and mass spectra are available on the Journal's website.

## Conflicts of Interest

The authors declare no conflicts of interest.

## Acknowledgements

We thank La Trobe University, The Australian Research Council (JLD, FT16010007) and The Australian Commonwealth (MA, Australian Postgraduate Award PhD scholarship) for their generous funding of this work.

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