**Reactions of trivalent iodine reagents with classic iridium and rhodium complexes.**

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**Abstract**

In this work, the reactions of iodine(III) reagents (PhI(L)2: L = pyridine, OAc-, 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 is observed.

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**Introduction**

Iodine(III) reagents with a PhI(L)2 motiff (L = -Cl, -OAc, pyridine) have attracted much attention as stoichiometric oxidants due 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 PhICl2 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]



Scheme 1. Oxidation of compound **1** using PhICl2 and PhI(OAc)2.

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 for 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]



Scheme 2. Reaction of compound **1** with dicationic I(III) reagents.

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**.



Scheme 3. Synthesis of Au(III) complex **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 18F- to generate complexesthat have potential to be used in PFT imaging.[15]



Scheme 4. Reaction of dicationic I(III) reagent with Pd(II).

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 this study we explore the reactions of selected phosphine containing Ir(I) and Rh(I) complexes with I(III) reagents containing anionic and neutral ligands (Figure 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]



Figure 1. Iridium(I), rhodium(I) and iodine(III) reagents used in this study.

**Experimental**

*Materials and Methods*

NMR solvents were purchased from Cambridge Isotope Laboratories and dried by stirring for 3 days over CaH2, which was distilled and stored over 3 Å molecular sieves in the glovebox. CH2Cl2, CH3CN, n-hexane, toluene and chloroform, which were purchased from Caledon Laboratories, were dried using an Innovative Technologies solvent purification system. All solvents were stored over 3 Å molecular sieves in nitrogen filled glovebox. All remaining reagents were ordered from Sigma-Aldrich and used as received. Ir(PPh3)2(CO)Cl,[18] Rh(PPh3)3Cl,[19] [Rh(dppe)2][Cl],[20] [PhI(Pyr)2][OTf]2and [PhI(4-DMAP)2][OTf]2[13]were prepared following published procedures. The metathesis to produce [Rh(dppe)2][OTf] was carried out by the addition of 1:1 stochiometric ratio of TMS-OTf to CH2Cl2 solution of [Rh(dppe)2][Cl] followed by solvent removal at reduced pressure.

CCDC numbers 1539214-1539218 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 CDCl3 was added drop wise to a solution of **9** (100 mg, 0.13 mmol) in 5 mL CDCl3 and stirred for 3 hours at room temperature. A color change from bright yellow to light yellow was observed within 10 minutes. The solvent was reduced to half under reduced pressure and 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 x 10mL) and dried under reduced pressure. 31P NMR (162 MHz, CDCl3) δ (ppm): 2.0 (s), -1.6 (s), -9.6 (s), -10.9 (s), -12.6, -13.7 (s). See the supporting information for the 1H NMR. ESI-MS of the identified compounds [M]n+ : 876.1 [Ir(PPh3)2(CO)(Cl)2(OAc)], 894.1 [Ir(PPh3)2(OAc)3].

*Reaction of* ***2R*** *with* ***9****.*

A solution of **2R** (0.13 mmol) in 5 mL CDCl3 was added drop wise to a solution of **9** (100 mg, 0.13 mmol) in 5 mL CDCl3 and stirred for 3 hours at room temperature. A color change from bright yellow to light yellow was observed within 30 minutes. The solvent was reduced to half under reduced pressure and 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 x 10mL) and dried under reduced pressure. **R = NMe2**: 31P NMR (162 MHz, CDCl3) δ (ppm): -2.4 (s), -8.4 (s), -15.4 (s). See the supporting information for the 1H NMR. ESI-MS [M]n+ : *m/z* 797.1 [Ir(PPh3)(CO)(Cl)2(DMAP)2]+, 937.0 [Ir(PPh3)2(CO)(Cl)2(DMAP)]+. **R = H**: 31P NMR (162 MHz, CDCl3) δ (ppm): 65.9 (s), 26.9 (s), -3.9 (s), -14.6 (s), -15.2 (s), -16.4 (s), -23.1 (s). ESI-MS [M]n+ : *m/z* 711.1 [Ir(PPh3)(CO)(Cl)2(Pyr)2]+, 894.1 [Ir(PPh3)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 CDCl3 was added drop wise to a solution of **9** (50 mg, 0.064 mmol) in 2 mL CDCl3. A color change from bright yellow to brown was observed in 10 min. An aliquot was removed for NMR and mass spectrometry analysis. 31P NMR (162 MHz, CDCl3) δ (ppm): 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). ESI-MS [M]n+ : *m/z* 745.2 [Ir(PPh3)2CO]+, 753.2 [Ir(PPh3)2Cl]+, 786.1 [Ir(PPh3)2Cl2]+, 803.1 [Ir(PPh3)2CO(OAc)]+, 839.1 [Ir(PPh3)2CO(OAc)Cl]+.

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

A solution of **2OAc** (35 mg, 0.11 mmol) in 2 mL CDCl3 was added drop wise to a solution of **10** (100 mg, 0.11 mmol) in 5 mL CDCl3 and stirred for 3 hours at room temperature. A color change from burgundy to light red was observed. The solvent was reduced to half under reduced pressure and 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 x 10mL) and dried under reduced pressure. 31P NMR (162 MHz, CDCl3) δ (ppm): 24.5 (d, J= 122 Hz). 1H NMR (400 MHz, CDCl3): δ (ppm): 7.43-7.38 (m, 6H), 7.37-7.32 (m, 12H), 7.20-7.17 (m, 12H), 2.08 (s, 3H). 13C NMR (100 MHz, CDCl3): δ (ppm): 191.24, 135.61, 130.94, 129.28, 127.71, 25.70. ESI-MS [M]n+ : *m/z* 721.1 [Rh(PPh3)2(Cl)(OAc)]+.

*Reaction of* ***2R*** *with* ***10****.*

A solution of **2R** (0.11 mmol) in 5 mL CDCl3 was added drop wise to a solution of **10** (100 mg, 0.11 mmol) in 5 mL CDCl3 and stirred for 3 hours at room temperature. A color change from burgundy to light red-brown was observed. The solvent was reduced to half under reduced pressure and 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 x 10mL) and dried under reduced pressure. **R = NMe2**: 31P NMR (162 MHz, CH2Cl2) δ (ppm): 28.2 (s), 14.1 (d, J= 88 *Hz*), 11.9 (d, J=88 *Hz).* ESI-MS [M]n+: *m/z* 803.0 [Rh(PPh3)(Cl)2(DMAP)3]+, 942.2 [Rh(PPh3)2(Cl)2(DMAP)2]+. **R = H**: 31P NMR (162 MHz, CH2Cl2) δ (ppm): 65.0 (s), 14.0 (d, J*=* 84 *Hz*), 9.7 (d, J*=* 104 *Hz*). ESI-MS [M]n+ : *m/z* 673.6 [Rh(PPh3)(Cl)2(Pyr)3]+, 854.9 [Rh(PPh3)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 CDCl3 was added drop wise to a solution of **10** (50 mg, 0.054 mmol) in 2 mL CDCl3. A color change from burgundy to brown was observed in 10 min. Aliquot was removed for NMR and mass spectrometry analysis. 31P NMR (162 MHz, CDCl3) δ (ppm): 61.9 (s), 45.2 (dt, J= 135 *Hz*), 23.4 (s), 19.8 (dt, J= 100 *Hz*). ESI-MS [M]n+ : *m/z* 297.1 [PPh3-Cl]+, 307.1 [Rh-IPh]+, 406.0 [Rh-PPh3-NCCH3]+, 477.0 [Rh-PPh3-Cl2-NCCH3]+, 568.9 [PPh3-Rh-I-Ph]+, 627.0 [Rh(PPh3)2]+, 697.0 [Rh(PPh3)2Cl2]+.

*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 CH2Cl2 was added drop wise to a solution of **11** (100 mg, 0.095 mmol) in 5 mL CH2Cl2 and stirred for one hour at room temperature. A color change from bright yellow to yellow was observed within 5 minutes. The solvent was reduced to half under reduced pressure and 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 x 10mL) and dried under reduced pressure (84 mg, 70% yield). 31P NMR (162 MHz, CH2Cl2): δ (ppm) 58.6 (dt, J= 11, 84 *Hz*), 42.5 (dt, J*=* 11, 115 *Hz*). 1H NMR (400 MHz, CD3CN) δ (ppm): 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). 13C NMR (100 MHz, CD3CN): δ (ppm): 172.07, 134.55, 134.08, 133.55, 133.25, 130.45, 130.24, 126.05, 125.51, 24.37, 20.22, 16.68. ESI-MS [M]n+ : *m/z* 479.1 [Rh(dppe)2(OAc)]2+.

*Reaction of* ***2NMe2*** *with* ***11****.*

A solution of **2NMe2** (72 mg, 0.095 mmol) in 5 mL CDCl3 was added drop wise to a solution of **11** (100 mg, 0.095 mmol) in 5 mL CDCl3 and stirred for 3 hours at room temperature. A color change from bright yellow to yellow was observed. The solvent was reduced to half under reduced pressure and 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 x 10mL) and dried under reduced pressure (80 mg, 53% crude yield). 31P NMR (162 MHz, CDCl3) δ (ppm): 30.8 (s), 40.7 (dt, J*=* 15, 113 *Hz*), 34.5 (dt, 15, 86 *Hz*). 1H NMR (400 MHz, CDCl3) δ (ppm): 7.98-6.65 (m, 50H), 3.19 (s, 12H). ESI-MS [M]n+ : *m/z* 380.7 [Rh(dppe)2(DMAP)2]3+, 510.1 [Rh(dppe)2(DMAP)]2+.

**Results and Discussion**

Treatment of **9** with **2OAc** in CDCl3 for three hours resulted in a pale yellow solution. The 31P NMR spectrum of the reaction mixture gave 6 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 vapor diffusion of Et2O into a concentrated CH2Cl2 solution of the mixture, which showed the crystals to be Ir(III) compounds **12** and **13** (Figure 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, 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/anion scrambling.[12, 21-22]

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

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

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

Treatment of **9** with **2NMe2** in CDCl3 at room temperature for 3 hours resulted in a color change from bright yellow to light yellow. The 31P NMR spectrum of the isolated solid in CDCl3 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 CH3CN solution of the isolated solid gave fragments that could be identified at [m/z]+ = 797.1 consistent with **14NMe2** and [m/z]+ = 937.1 consistent with **15NMe2** as shown in Scheme 6. The stereochemistry of **14NMe2** cannot be determined from the data. The presence of one unique P environment in **15NMe2** inferred by the lack of P-P coupling allows for the assignment of PPh3 ligands as trans to one another, but the configuration of the other ligands relative to each other cannot be determined.



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

X-Ray diffraction studies were done on single crystals obtained from vapor diffusion of Et2O into concentrated CH2Cl2 solution of the isolated solid which revealed compound **16.** This compound has been synthesized previously via reacting IrCl(PPh3)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 31P 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 chlorophosphonium cation ([Ph3PCl]+)[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/anion scrambling.

The reaction of **10** with **2OAc** in CDCl3 at room temperature for 3 hours resulted in a color change to light reddish brown. The 31P 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 with 103Rh, which suggests the presence of two compounds, each with one unique 31P environment.



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

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 CH2Cl2 and placed at -35 ºC overnight. The solid then was filtered and washed with n-hexane. X-Ray diffraction studies performed on single crystals obtained from concentrated CH2Cl2 solution of the isolated solid at -35 ºC confirmed product **17** as shown in Figure 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.

Rh_Cl2_PPh3_OAc%20copy.pdf

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

The drop wise addition of **2NMe2** to **10** at room temperature in CDCl3 resulted in a color change from burgundy to light red over 3 hours. The 31P 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 [m/z]+= 803.0 which also were 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 31P NMR spectroscopy. As with the reaction of **9** with **2H**, the 31P NMR also contained a singlet at 65.0 ppm indicating the presence of the chlorophosphonium cation [Ph3PCl]+. 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.



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

The slow addition of **2OAc.OTf** to **10** in 1:1 ratio resulted in color change from burgundy to brown within 10 min. The 31P NMR of the reaction mixture had four signals between 4 and 62 ppm. The major singlet at 62 ppm represents the chlorophosphonium cation [Ph3PCl]+ 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 *m/z* = [697.1] which were assigned to [Rh(PPh3)(Ph)(I)]+ and [Rh(PPh3)2(Cl)2]+ respectively. The former product indicates that it is possible for the I-Ph fragment of the iodine(III) oxidant to 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 PhIL2 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 CDCl3 at room temperature for 3 hours resulted in no color change. The 31P 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 drop wise addition of a CH2Cl2 solution containing PhI(OAc)(OTf) and TMS-OTf to compound **11** resulted in a color change from bright yellow to yellow which gave a yellow solid after a short workup. The positive ESI-MS spectrum of the isolated solid re-dissolved in CH3CN showed a major peak at [m/z]+= 479.1 with a half mass unit peak separation which 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 Figure 4, with the two dppe ligands retained.



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

MA_Rh_dppe_OAc_thesis%20copy.pdf

Figure 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 CDCl3 at room temperature for 3 hours followed by workup resulted in the isolation of a yellow solid. The 31P 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 detection 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 an 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 31P NMR, bearing in mind the semi-quantitative nature of 31P NMR. A battery of efforts to selectively precipitate **22** to obtain an analytically pure sample unfortunately failed.



Scheme 10. Outcomes of the reaction of **11** with **2NMe2** as identified by mass spectrometry.

**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 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, and 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.

**Supplementary Material**

Experimental details, 1H, 31P NMR spectra, and mass spectra. X-ray crystallographic details (CIF).

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**TOC Figure and Synopsis**



The reactions of classic iridium and rhodium complexes with iodine (III) oxidants are described. All reactions resulted in two-electron oxidation of the metal centre. Ligand exchange and anion scrambling was observed in monodentate ligand containing complexes. In the case of reacting I(III) reagents with chelating ligand containing complex, no scrambling is observed leading to the isolation of well-defined complexes.