Supplementary Material

Reactions of trivalent iodine reagents with classic iridium and rhodium complexes

Mohammad AlbayerA and Jason L. DuttonA,B

ADepartment of Chemistry and Physics, La Trobe Institute for Molecular Science, La Trobe University, Melbourne, Vic. 3086, Australia.

BCorresponding author. Email: j.dutton@latrobe.edu.au

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], [Rh(PPh₃)₃Cl], [Rh(dppe)₂]Cl, [PhI(Pyr)₂][OTf]₂ and [PhI(4-DMAP)₂][OTf]₂ were prepared following published procedures.
The metathesis to produce [Rh(dppe)$_2$]OTf was carried out by the addition of 1:1 stoichiometric ratio of TMS-Triflate to CH$_2$Cl$_2$ solution of [Rh(dppe)$_2$]Cl followed by solvent removal at reduced pressure.

**X-ray Crystallography Details**

Single crystals were selected under n-paratone oil, mounted on nylon loops and placed into a cold stream (172 K) of N$_2$ on an Oxford CCD diffractometer using Mo Kα radiation. Structure solution and refinement were performed using the SHELXTL suite of software.

**Reaction of 2OAc with 9.**

A solution of 2OAc (42 mg, 0.13 mmol) in 2 mL CDCl$_3$ was added drop wise to a solution of 9 (100 mg, 0.13 mmol) in 5 mL CDCl$_3$ 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. $^3$P NMR (162 MHz, CDCl$_3$) δ (ppm): 2.0 (s), -1.6 (s), -9.6 (s), -10.9 (s), -12.0, -13.7 (s). See Figure 2 for the $^1$H NMR spectrum. The ESI-MS of the identified compounds [M]$^{n+}$: m/z 876.1 [Ir(PPh$_3$)$_2$(CO)(Cl)$_2$(OAc)$_3$], 894.1 [Ir(PPh$_3$)$_2$(OAc)$_3$].
Figure 1. Reaction of 2OAc with 9 $^{31}$P NMR.

Figure 2. Reaction of 2OAc with 9 $^1$H NMR.
Figure 3. Reaction of 2OAc with 9 ESI mass spectrum.

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 Figure 5 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)(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)]⁺.
Figure 4. Reaction of 2NMe₂ with 9³¹P NMR.
Figure 5. Reaction of $2\text{NMe}_2$ with $9$ $^1$H NMR.

Figure 6. Reaction of $2\text{NMe}_2$ with $9$ ESI mass spectrum.
Reaction of 2H with 9 \(^{31}\)P NMR.

![Figure 7](image)

Figure 7. Reaction of 2H with 9 \(^{31}\)P NMR.

Reaction of 2OAc.OTf with 9.

A mixture of 2OAc (20.6 mg, 0.064 mmol) and TMS-OTf (23.3 µL, 0.128 mmol) in 2 mL CDCl\(_3\) was added drop wise to a solution of 9 (50 mg, 0.064 mmol) in 2 mL CDCl\(_3\). A color change from
bright yellow to brown was observed in 10 min. Aliquot was removed for NMR and mass spectrometry analysis. $^31$P NMR (162 MHz, CDCl$_3$) $\delta$ (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(PPh$_3$)$_2$CO]$^+$, 753.2 [Ir(PPh$_3$)$_2$Cl]$^+$, 786.1 [Ir(PPh$_3$)$_2$Cl$_2$]$^+$, 803.1 [Ir(PPh$_3$)$_2$CO(OAc)]$^+$, 839.1 [Ir(PPh$_3$)$_2$CO(OAc)Cl]$^+$.

Figure 9. Reaction of 2OAc.OTf with 9 $^31$P NMR.

Figure 10. Reaction of 2OAc.OTf with 9 ESI mass spectrum.
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]⁺ : m/z 721.1 [Rh(PPh₃)₂(Cl)(OAc)]⁺.

Figure 11. Isolated solid from the reaction of 2OAc with 10 ³¹P NMR.
Figure 12. Reaction of 2OAc with 10 $^1$H NMR.

Figure 13. Reaction of 2OAc with 10 $^{13}$C NMR.
Reaction of \(\textbf{2OAc}\) with \(\textbf{10}\) ESI mass spectrum.

**Reaction of \(\textbf{2R}\) with Wilkinson’s catalyst (\(\textbf{10}\)).**

A solution of \(\textbf{2R}\) (0.11 mmol) in 5 mL CDCl\(_3\) was added drop wise to a solution of \(\textbf{10}\) (100 mg, 0.11 mmol) in 5 mL CDCl\(_3\) 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. \(\textbf{R} = \text{NMe}_2\): \(^{31}\text{P}\) NMR (162 MHz, CH\(_2\)Cl\(_2\))  \(\delta\) (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(PPh\(_3\))(Cl)\(_2\)(DMAP)\(_3\)]\(^+\), 942.2 [Rh(PPh\(_3\))\(_2\)(Cl)\(_2\)(DMAP)\(_2\)]\(^+\). \(\textbf{R} = \text{H}: \) \(^{31}\text{P}\) NMR (162 MHz, CH\(_2\)Cl\(_2\))  \(\delta\) (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(PPh\(_3\))(Cl)\(_2\)(Pyr)\(_3\)]\(^+\), 854.9 [Rh(PPh\(_3\))\(_2\)(Cl)\(_2\)(Pyr)\(_2\)]\(^+\).
Figure 15. Reaction of $2\text{NMe}_2$ with $10$ $^{31}\text{P}$ NMR.

Figure 16. Reaction of $2\text{NMe}_2$ with $10$ ESI mass spectrum.
Reaction of $2\text{H}$ with $10$.  

A mixture of $2\text{OAc} \cdot \text{OTf}$ (17.4 mg, 0.054 mmol) and TMS-OTf (19.7 µL, 0.108 mmol) in 2 mL CDCl$_3$ was added drop wise to a solution of $10$ (50 mg, 0.054 mmol) in 2 mL CDCl$_3$. A color change from
burgundy to brown was observed in 10 min. Aliquot was removed for NMR and mass spectrometry analysis. $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ (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 [PPh$_3$-Cl]$^+$, 307.1 [Rh-I-Ph]$^+$, 406.0 [Rh-PPh$_3$-NCCH$_3$]$^+$, 477.0 [Rh-PPh$_3$-Cl$_2$-NCCH$_3$]$^+$, 568.9 [PPh$_3$-Rh-I-Ph]$^+$, 627.0 [Rh(PPh$_3$)$_2$]$^+$, 697.0 [Rh(PPh$_3$)$_2$Cl$_2$]$^+$.

Figure 19. Reaction of 2OAc.OTf with 10 $^{31}$P NMR.

Figure 20. Reaction of 2OAc.OTf with 10 ESI mass spectrum.
Reaction of 2OAc.OTf 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]⁺: m/z 479.1 [Rh(dppe)₂(OAc)]²⁺.

Figure 21. Reaction of 2OAc.OTf with 11. ³¹P NMR.
Figure 22. Reaction of $2OAc$ with $11$ $^1H$ NMR.

Figure 23. Reaction of $2OAc$ with $11$ $^{13}C$ NMR.
Reaction of $\text{2OAc}$ with $\text{11}$ ESI mass spectrum.

**Reaction of $\text{2NMe}_2$ with $\text{11}$**.

A solution of $\text{2NMe}_2$ (72 mg, 0.095 mmol) in 5 mL CDCl$_3$ was added drop wise to a solution of $\text{11}$ (100 mg, 0.095 mmol) in 5 mL CDCl$_3$ 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. $^{31}$P NMR (162 MHz, CH$_2$Cl$_2$) $\delta$ (ppm) 40.7 (dt, J = 15, 113 Hz), 34.5 (dt, 15, 86 Hz). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.98-6.65 (m, 50H), 3.19 (s, 12H). ESI-MS [M]$^{n+}$ : m/z 380.7 [$\text{Rh(dppe)}_2(\text{DMAP})_2$]$^{3+}$, 510.1 [$\text{Rh(dppe)}_2(\text{DMAP})$]$^{2+}$. 
Figure 25. Reaction of $2\text{NMe}_2$ with $11^{31}\text{P}$ NMR.
Figure 26. Reaction of 2NMe₂ with 11 ¹H NMR.

Figure 27. Reaction of 2NMe₂ with 11 ESI mass spectrum.
References: