10.1071/CH17173_AC

Australian Journal of Chemistry 2017, 70(11), 1180-1187

Supplementary Material

Reactions of trivalent iodine reagents with classic iridium and rhodium complexes

Mohammad Albayer[A] and Jason L. Dutton[A,B]

[A]Department of Chemistry and Physics, La Trobe Institute for Molecular Science, La Trobe University, Melbourne, Vic. 3086, Australia.

[B]Corresponding 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 CaH_2, which was distilled and stored over 3 Å molecular sieves in the 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 stored over 3 Å molecular sieves in nitrogen filled glovebox. All remaining reagents were ordered from Sigma-Aldrich and used as received. $[Ir(PPh_3)_2(CO)Cl]$,[1] $[Rh(PPh_3)_3Cl]$,[2] $[Rh(dppe)_2]Cl$,[3] $[PhI(Pyr)_2][OTf]_2$ and $[PhI(4\text{-}DMAP)_2][OTf]_2$[4] 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-Triflate to CH_2Cl_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. ^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm): 2.0 (s), -1.6 (s), -9.6 (s), -10.9 (s), -12.6, -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 $[Ir(PPh_3)_2(CO)(Cl)_2(OAc)]$, 894.1 $[Ir(PPh_3)_2(OAc)_3]$.

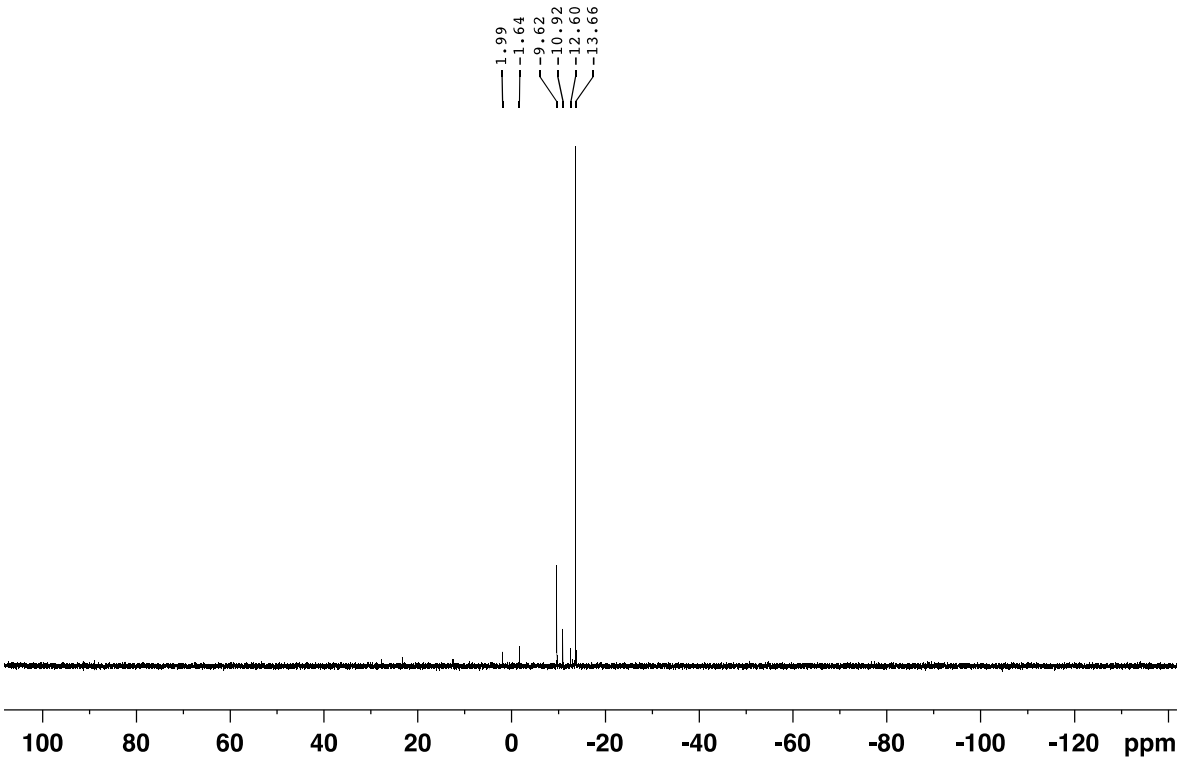

Figure 1. Reaction of **2OAc** with **9** ^{31}P NMR.

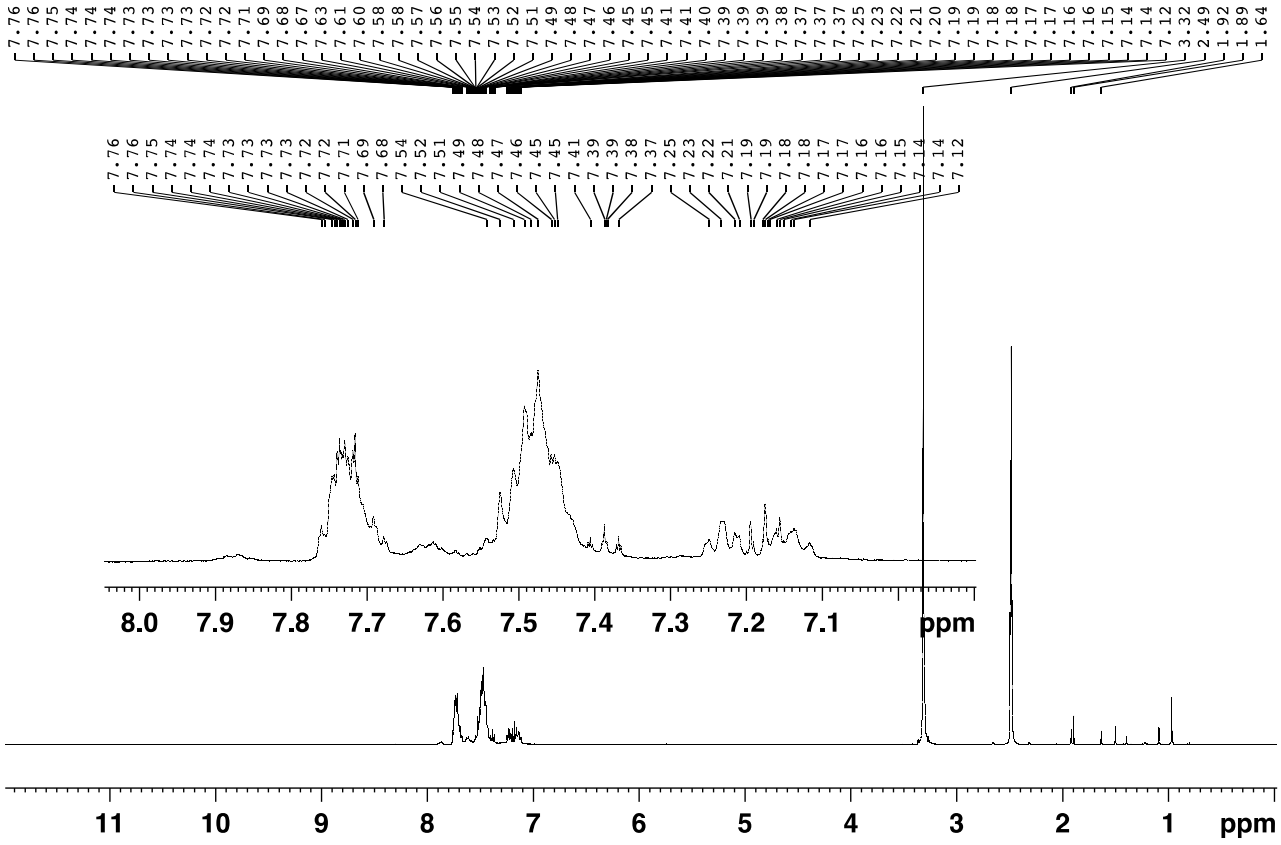

Figure 2. Reaction of **2OAc** with **9** ^{1}H NMR.

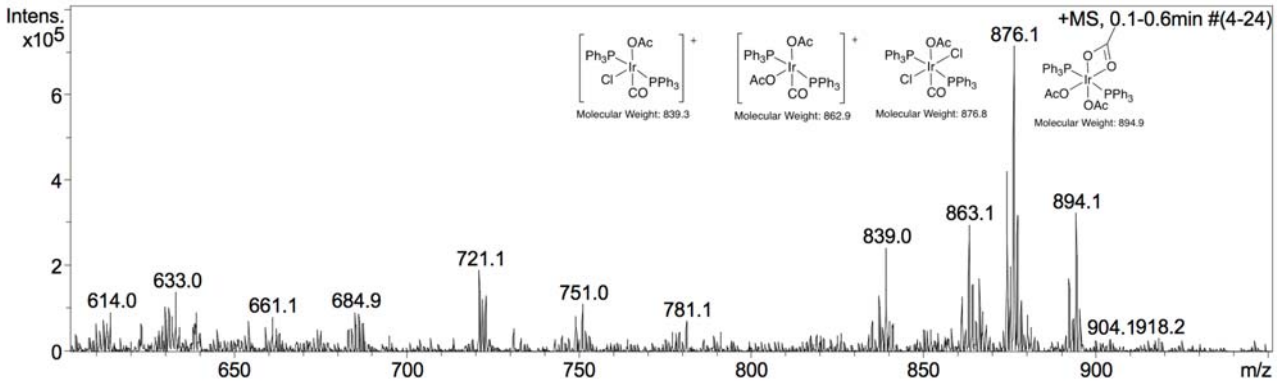

Figure 3. Reaction of **2OAc** with **9** ESI mass spectrum.

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

A solution of **2R** (0.13 mmol) in 5 mL $CDCl_3$ 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 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 = NMe_2**: ^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm): -2.4 (s), -8.4 (s), -15.4 (s). See Figure 5 for the ^{1}H NMR. ESI-MS $[M]^{n+}$: *m/z* 797.1 $[Ir(PPh_3)(CO)(Cl)_2(DMAP)_2]^+$, 937.0 $[Ir(PPh_3)_2(CO)(Cl)_2(DMAP)]^+$. **R = H**: ^{31}P NMR (162 MHz, $CDCl_3$) 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 $[Ir(PPh_3)(CO)(Cl)_2(Pyr)_2]^+$, 894.1 $[Ir(PPh_3)_2(CO)(Cl)_2(Pyr)]^+$.

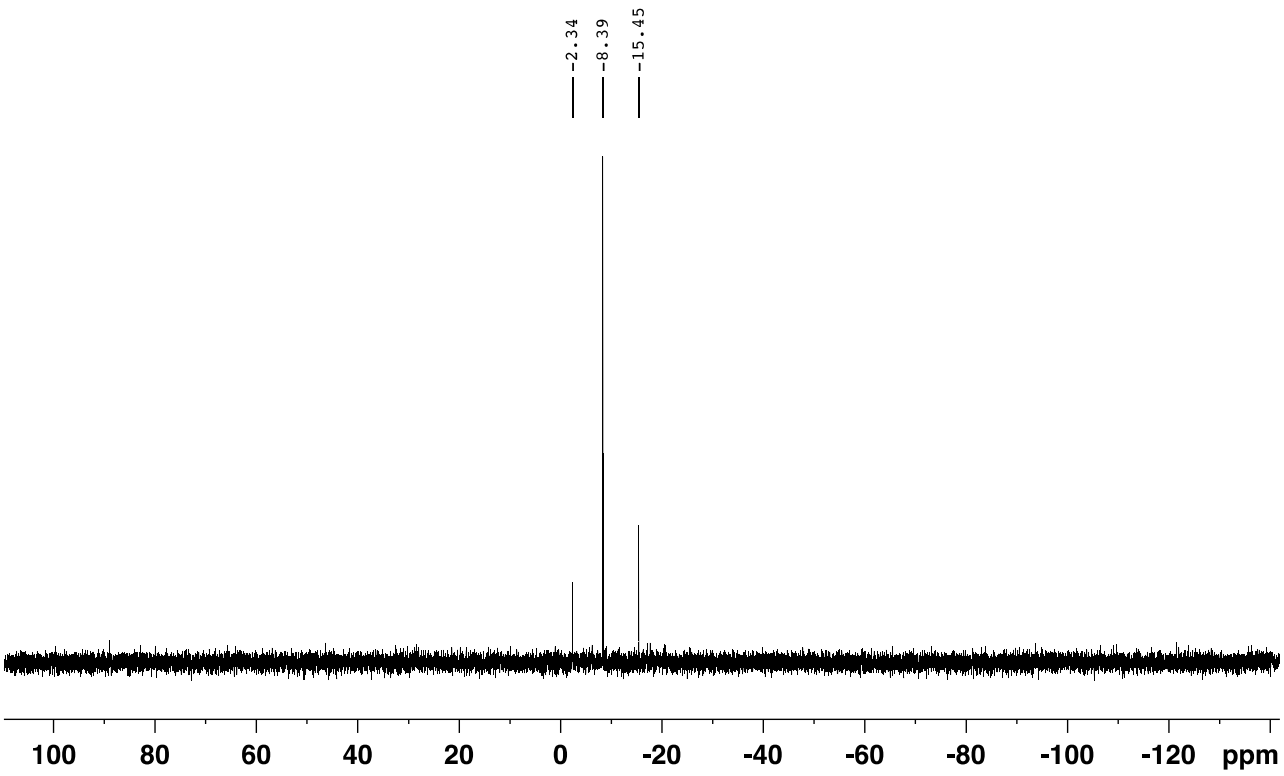

Figure 4. Reaction of **2NMe$_2$** with **9** ^{31}P NMR.

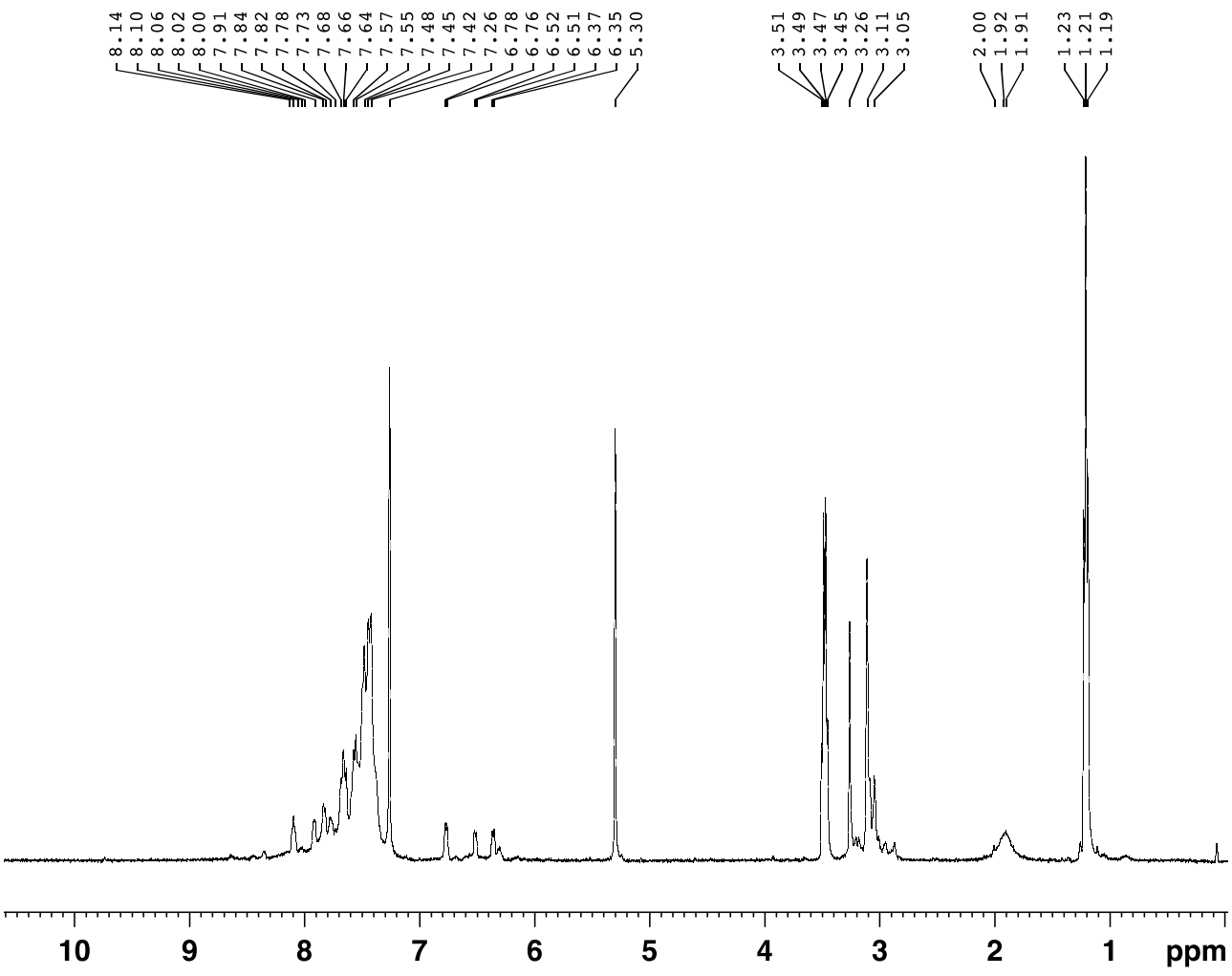

Figure 5. Reaction of **2NMe$_2$** with **9** ^{1}H NMR.

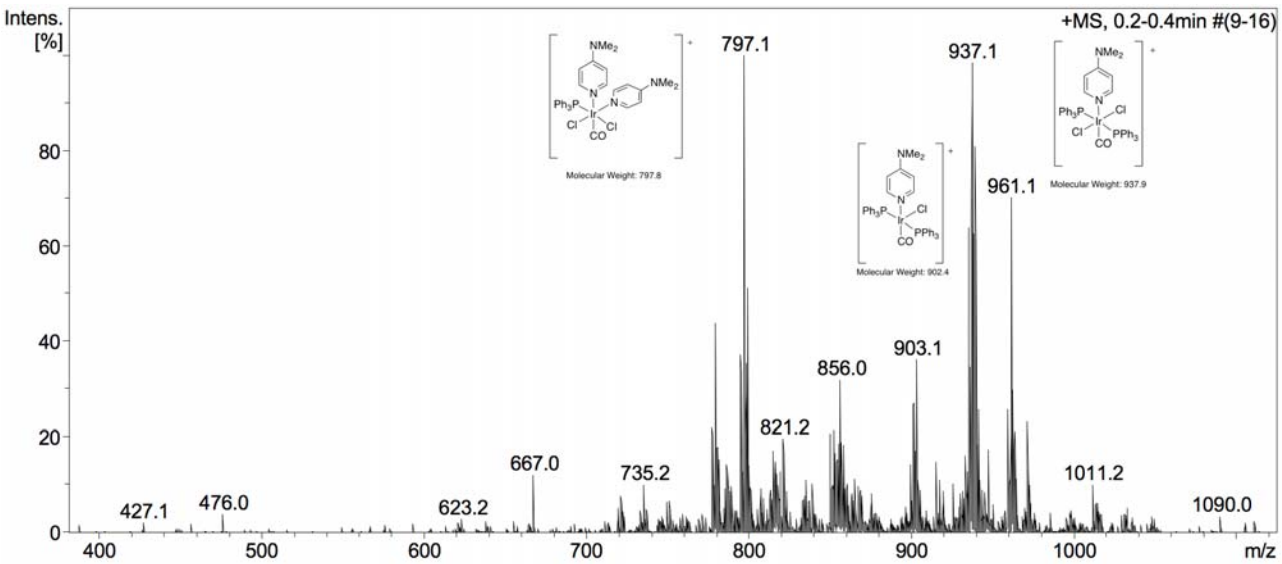

Figure 6. Reaction of **2NMe$_2$** with **9** ESI mass spectrum.

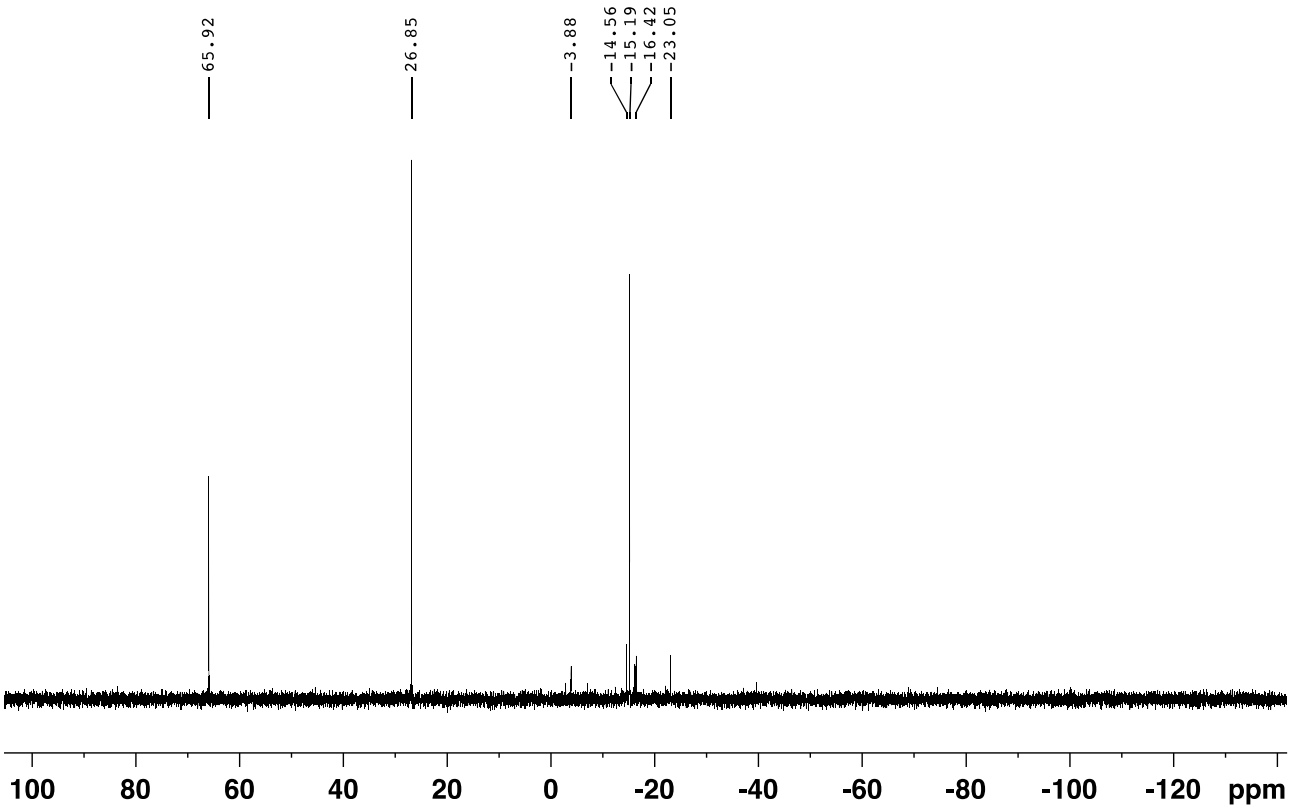

Figure 7. Reaction of **2H** with **9** ^{31}P NMR.

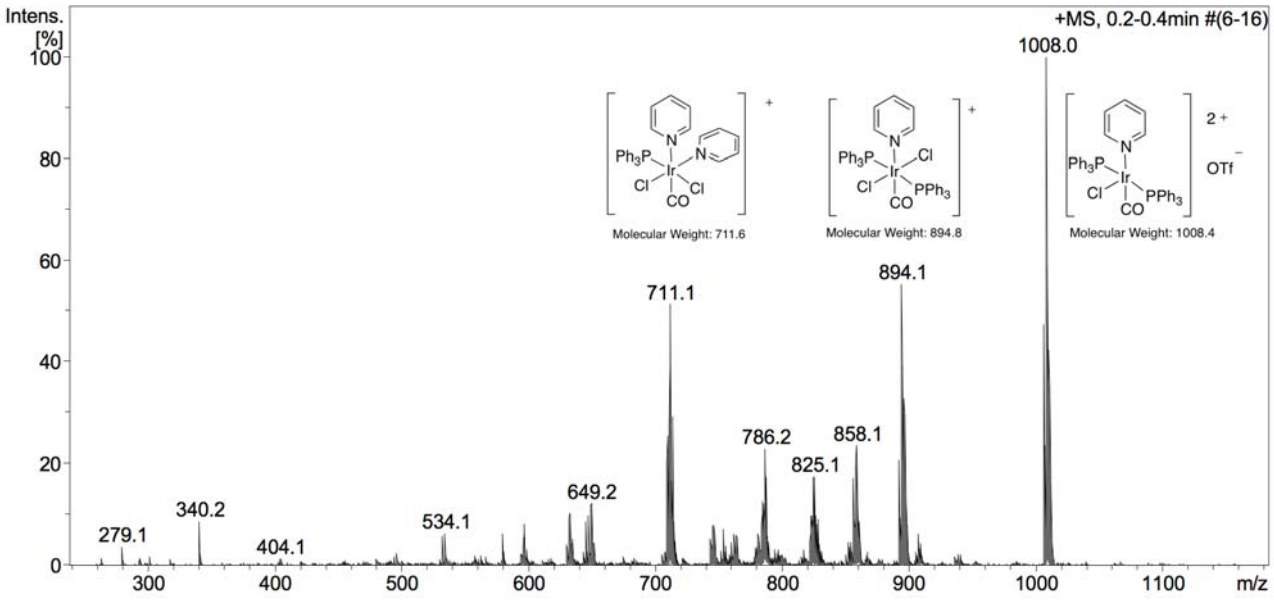

Figure 8. Reaction of **2H** with **9** ESI mass spectrum.

*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, $CDCl_3$) 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 $[Ir(PPh_3)_2CO]^+$, 753.2 $[Ir(PPh_3)_2Cl]^+$, 786.1 $[Ir(PPh_3)_2Cl_2]^+$, 803.1 $[Ir(PPh_3)_2CO(OAc)]^+$, 839.1 $[Ir(PPh_3)_2CO(OAc)Cl]^+$.

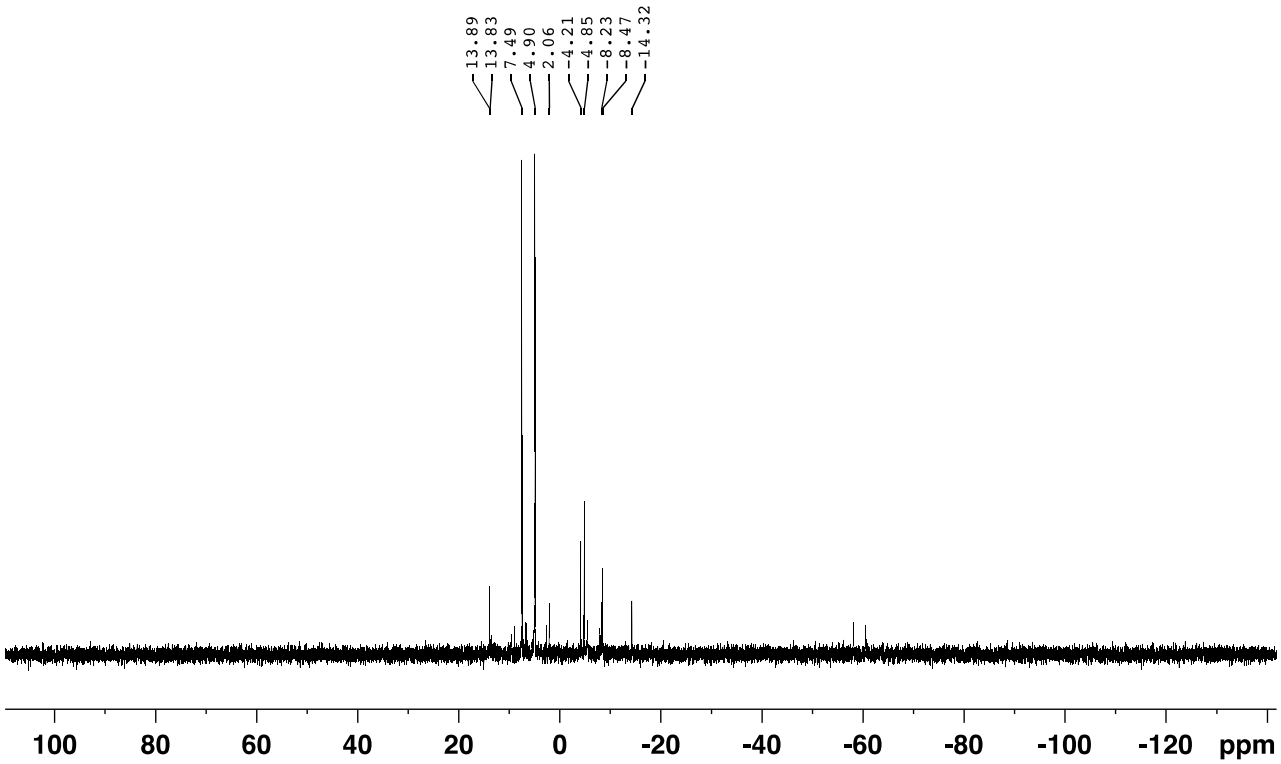

Figure 9. Reaction of **2OAc.OTf** with **9** ^{31}P NMR.

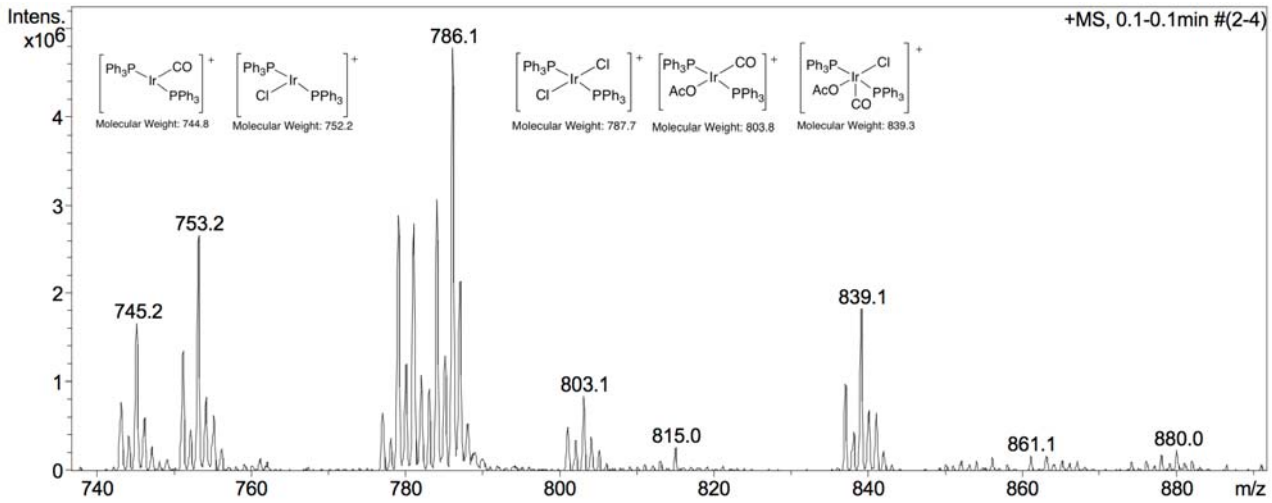

Figure 10. Reaction of **2OAc.OTf** with **9** ESI mass spectrum.

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

A solution of **2OAc** (35 mg, 0.11 mmol) in 2 mL $CDCl_3$ was added drop wise to a solution of **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 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. ^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm): 24.5 (d, J= 122 Hz). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.43-7.38 (m, 6H), 7.37-7.32 (m, 12H), 7.20-7.17 (m, 12H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 191.24, 135.61, 130.94, 129.28, 127.71, 25.70. ESI-MS $[M]^{n+}$: *m/z* 721.1 $[Rh(PPh_3)_2(Cl)(OAc)]^+$.

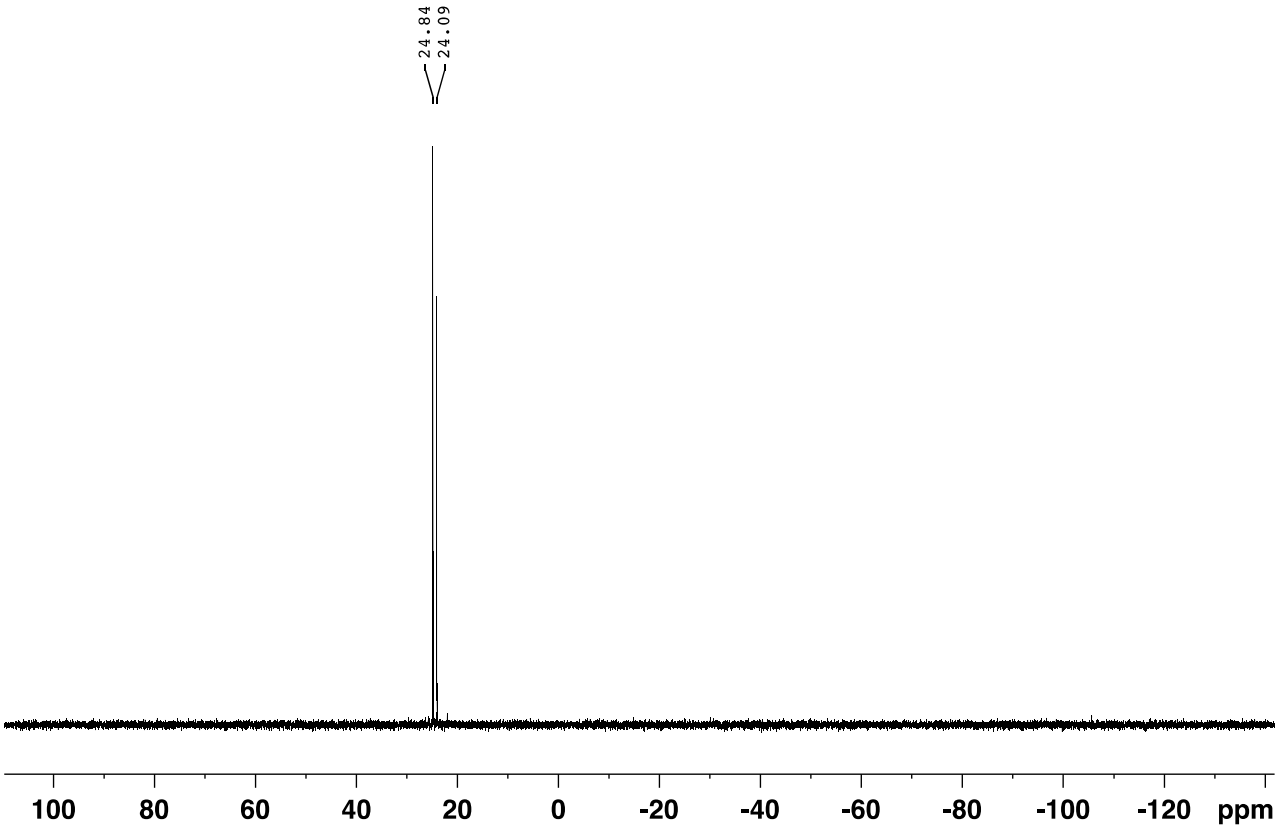

Figure 11. Isolated solid from the reaction of **2OAc** with **10** ^{31}P NMR.

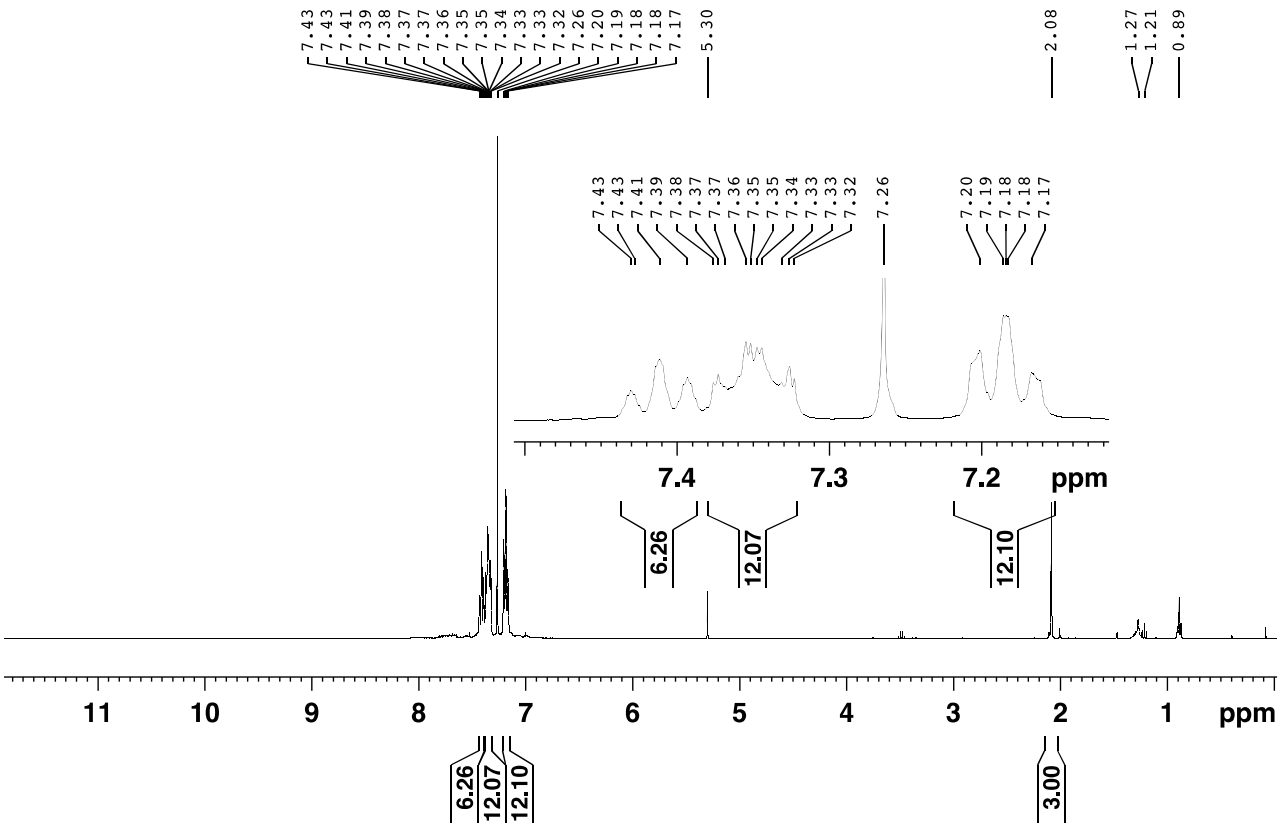

Figure 12. Reaction of **2OAc** with **10** ^{1}H NMR.

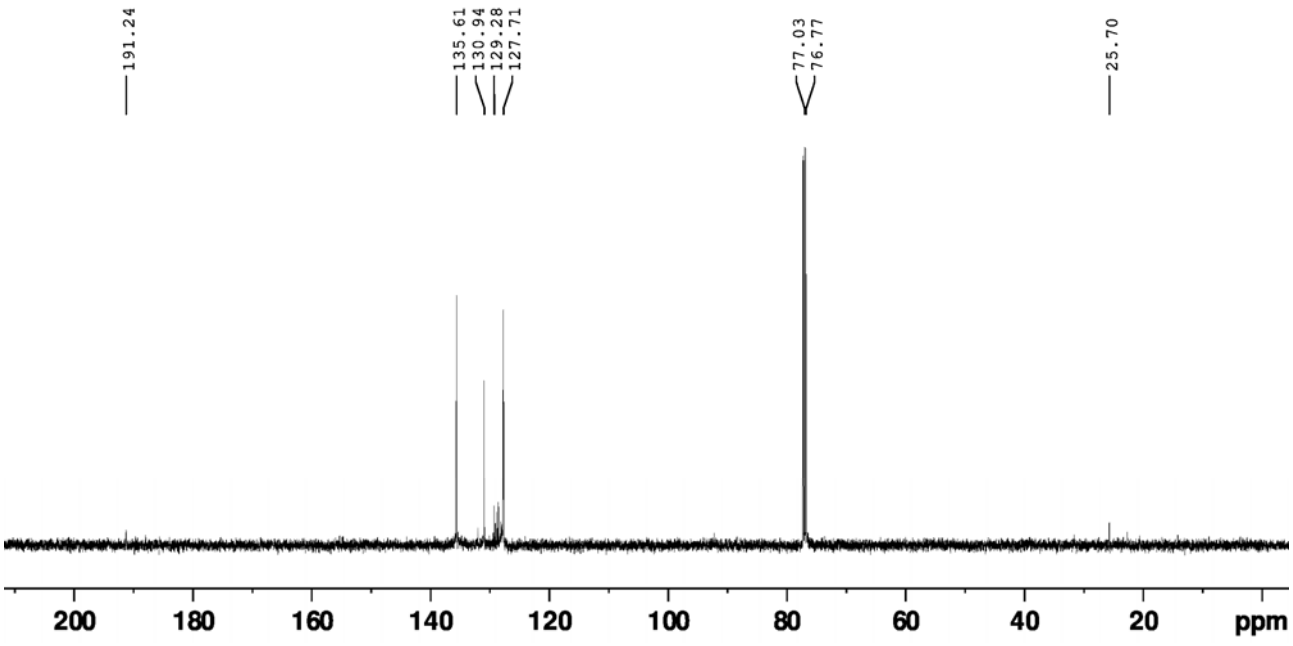

Figure 13. Reaction of **2OAc** with **10** ^{13}C NMR.

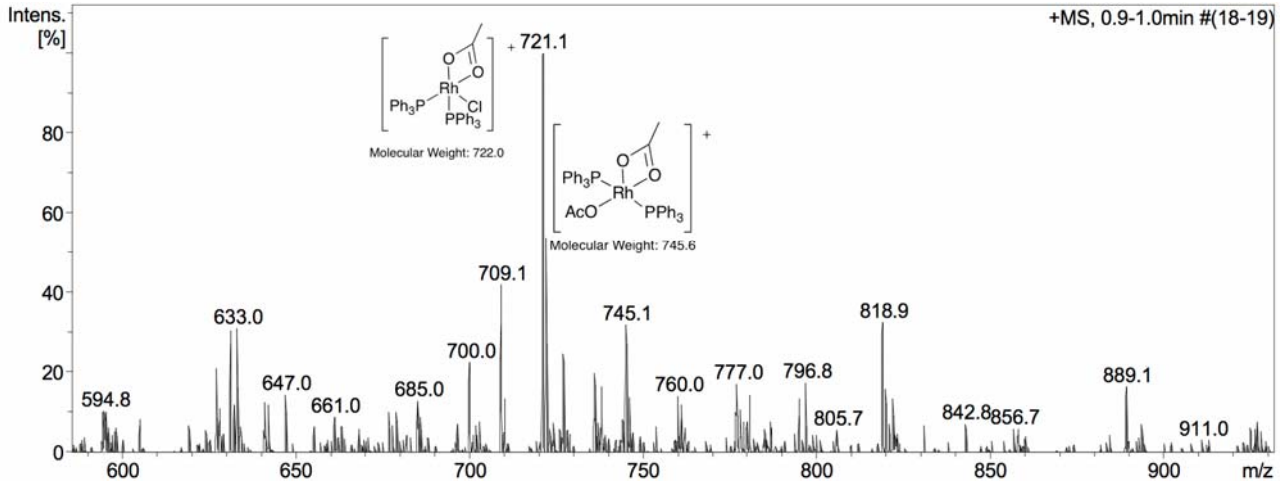

Figure 14. Reaction of **2OAc** with **10** ESI mass spectrum.

*Reaction of **2R** with Wilkinson's catalyst (**10**).*

A solution of **2R** (0.11 mmol) in 5 mL $CDCl_3$ was added drop wise to a solution of **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. **R = NMe_2**: ^{31}P NMR (162 MHz, CH_2Cl_2) 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 $[Rh(PPh_3)(Cl)_2(DMAP)_3]^+$, 942.2 $[Rh(PPh_3)_2(Cl)_2(DMAP)_2]^+$. **R = H**: ^{31}P NMR (162 MHz, CH_2Cl_2) 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 $[Rh(PPh_3)(Cl)_2(Pyr)_3]^+$, 854.9 $[Rh(PPh_3)_2(Cl)_2(Pyr)_2]^+$.

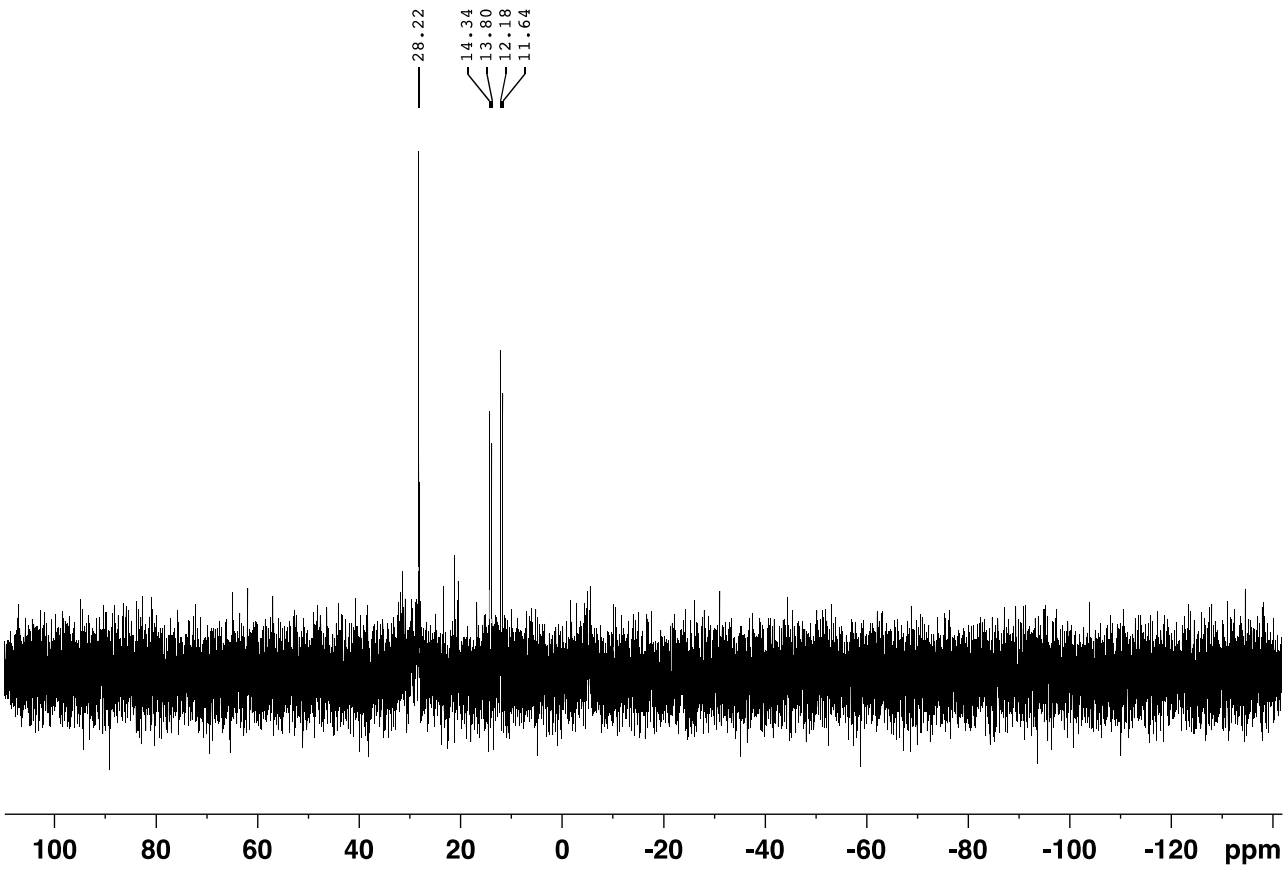

Figure 15. Reaction of **2NMe$_2$** with **10** ^{31}P NMR.

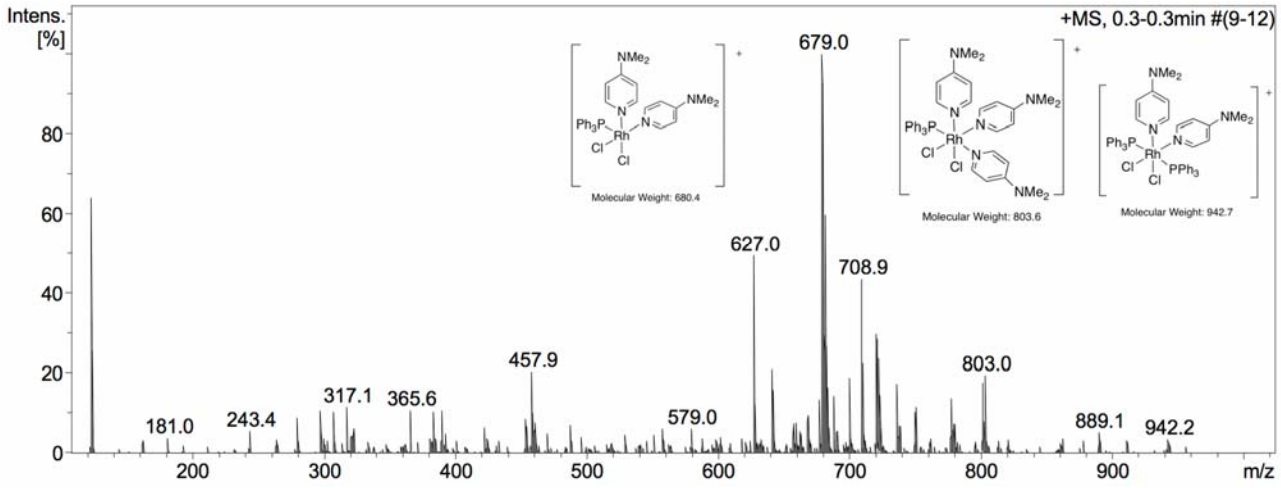

Figure 16. Reaction of **2NMe$_2$** with **10** ESI mass spectrum.

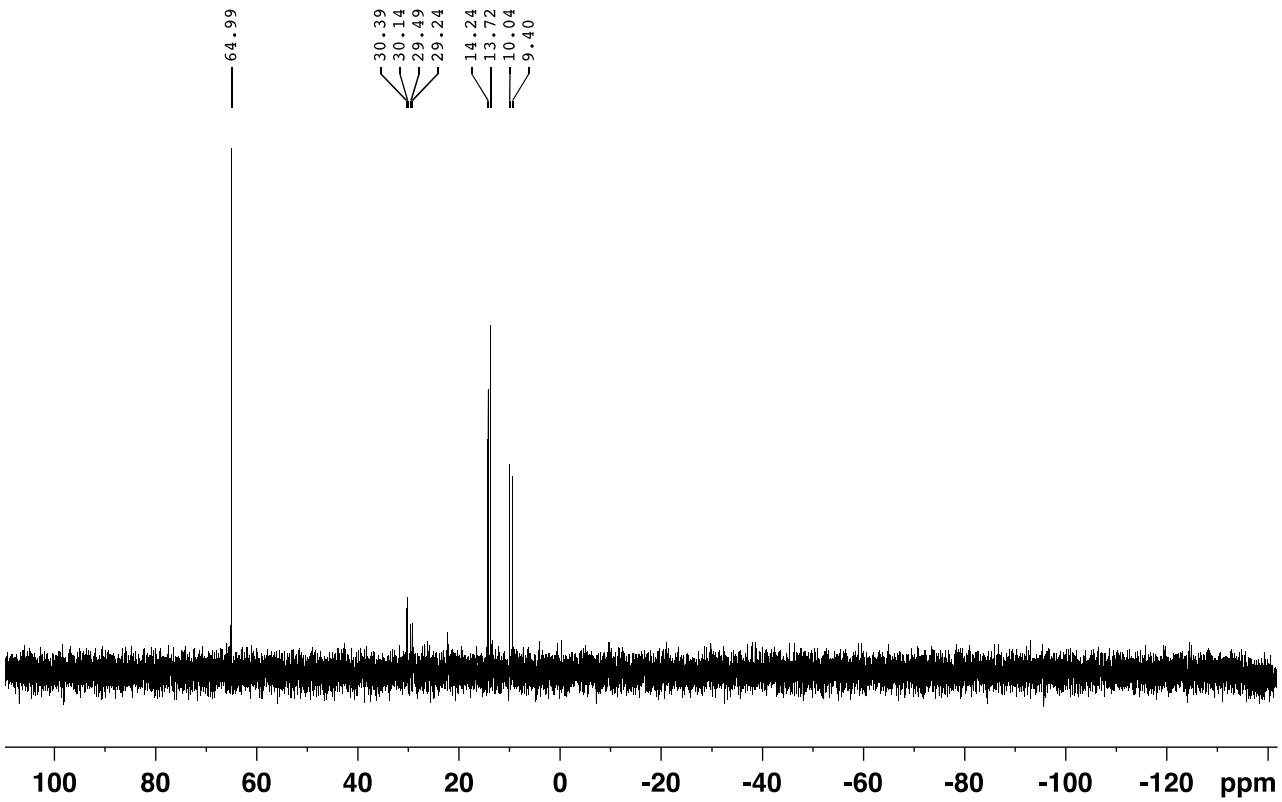

Figure 17. Reaction of **2H** with **10** ^{31}P NMR.

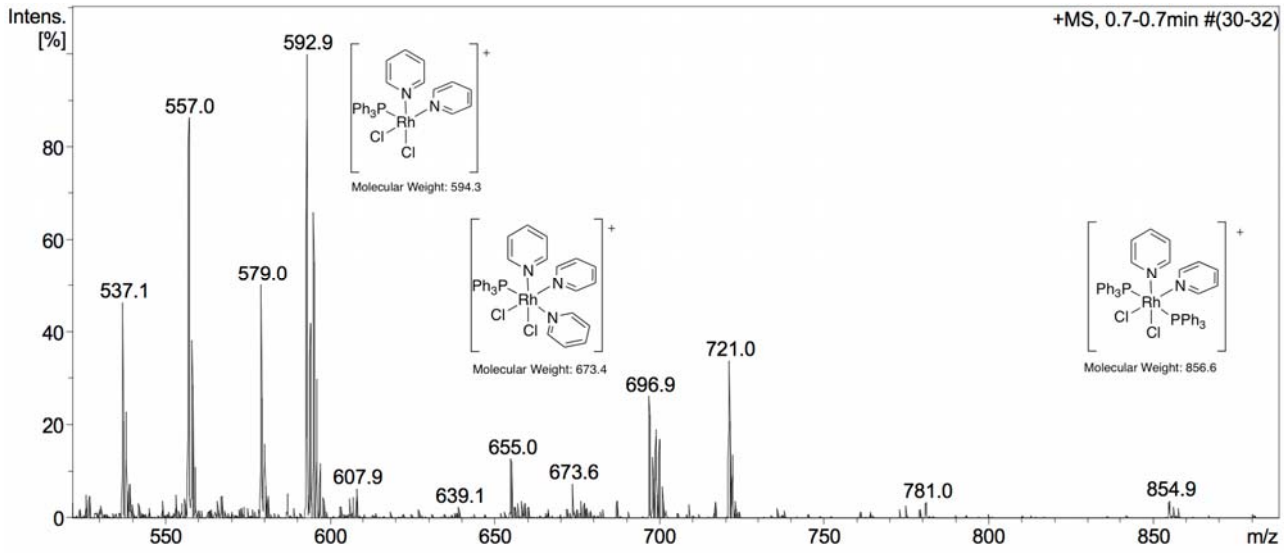

Figure 18. Reaction of **2H** with **10** ESI mass spectrum.

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

A mixture of **2OAc** (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, $CDCl_3$) 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 $[PPh3\text{-}Cl]^+$, 307.1 $[Rh\text{-}I\text{-}Ph]^+$, 406.0 $[Rh\text{-}PPh_3\text{-}NCCH_3]^+$, 477.0 $[Rh\text{-}PPh_3\text{-}Cl_2\text{-}NCCH_3]^+$, 568.9 $[PPh_3\text{-}Rh\text{-}I\text{-}Ph]^+$, 627.0 $[Rh(PPh_3)_2]^+$, 697.0 $[Rh(PPh_3)_2Cl_2]^+$.

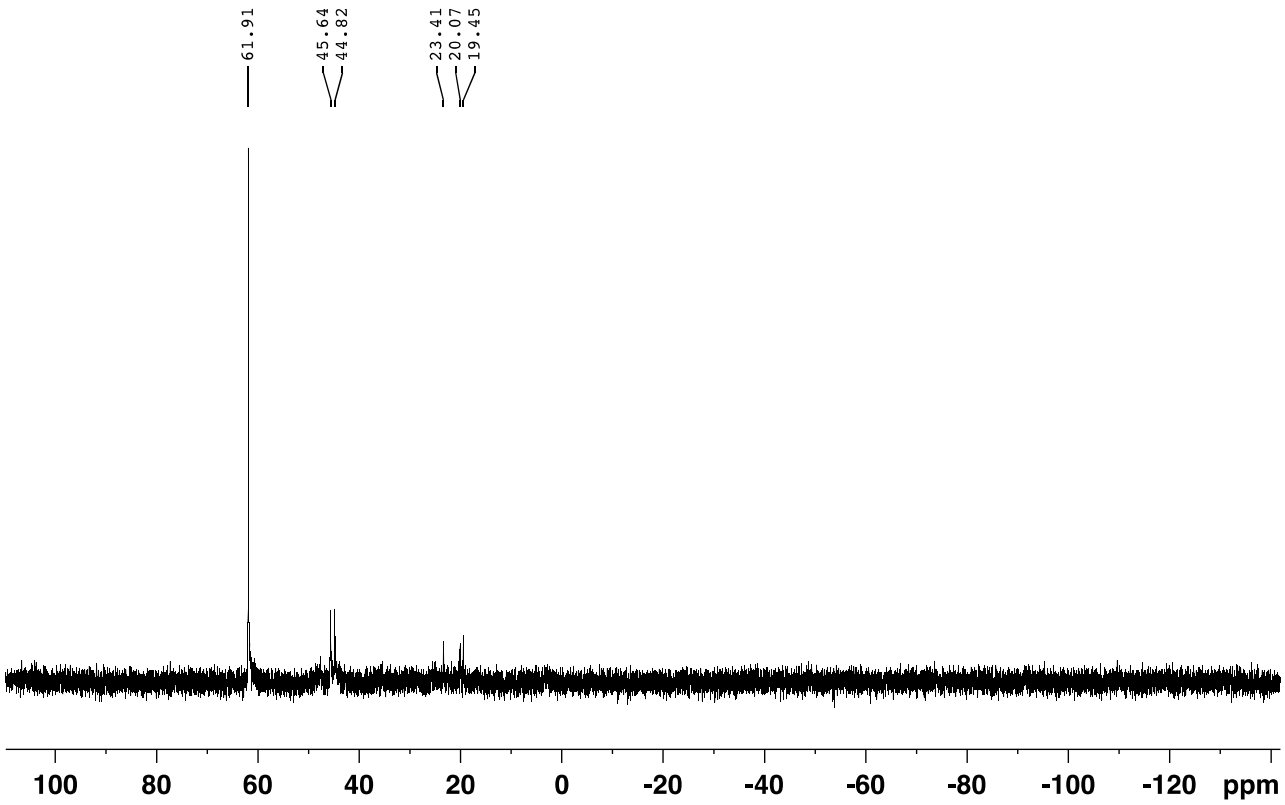

Figure 19. Reaction of **2OAc.OTf** with **10** ^{31}P NMR.

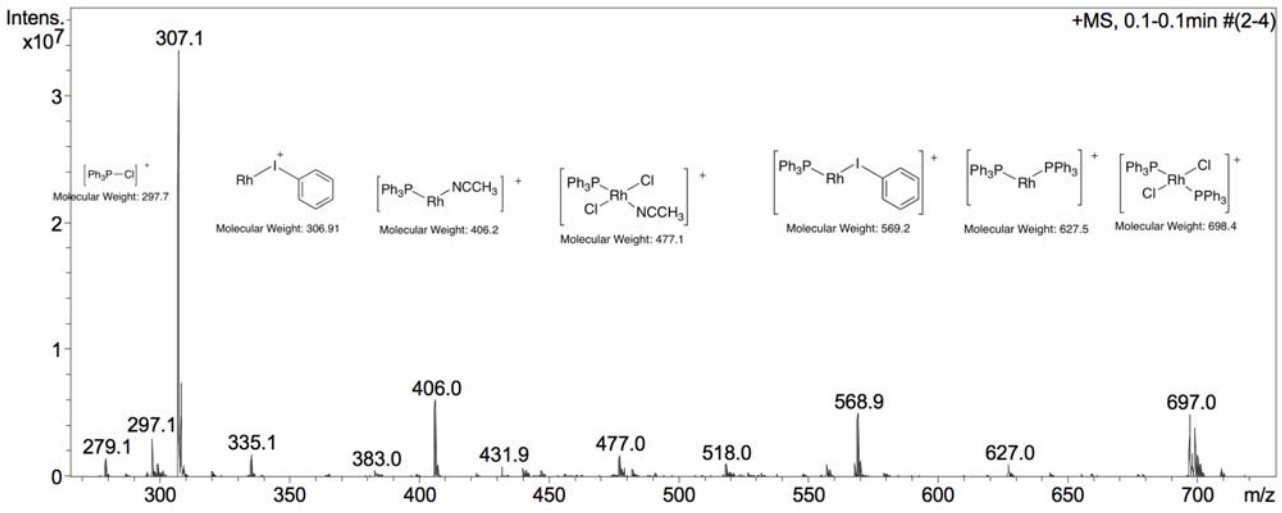

Figure 20. Reaction of **2OAc.OTf** with **10** ESI mass spectrum.

*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 CH_2Cl_2 was added drop wise to a solution of **11** (100 mg, 0.095 mmol) in 5 mL CH_2Cl_2 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). ^{31}P NMR (162 MHz, CH_2Cl_2): δ (ppm) 58.6 (dt, J= 11, 84 *Hz*), 42.5 (dt, J= 11, 115 *Hz*). ^{1}H NMR (400 MHz, CD_3CN) 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). ^{13}C NMR (100 MHz, CD_3CN): 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 $[Rh(dppe)_2(OAc)]^{2+}$.

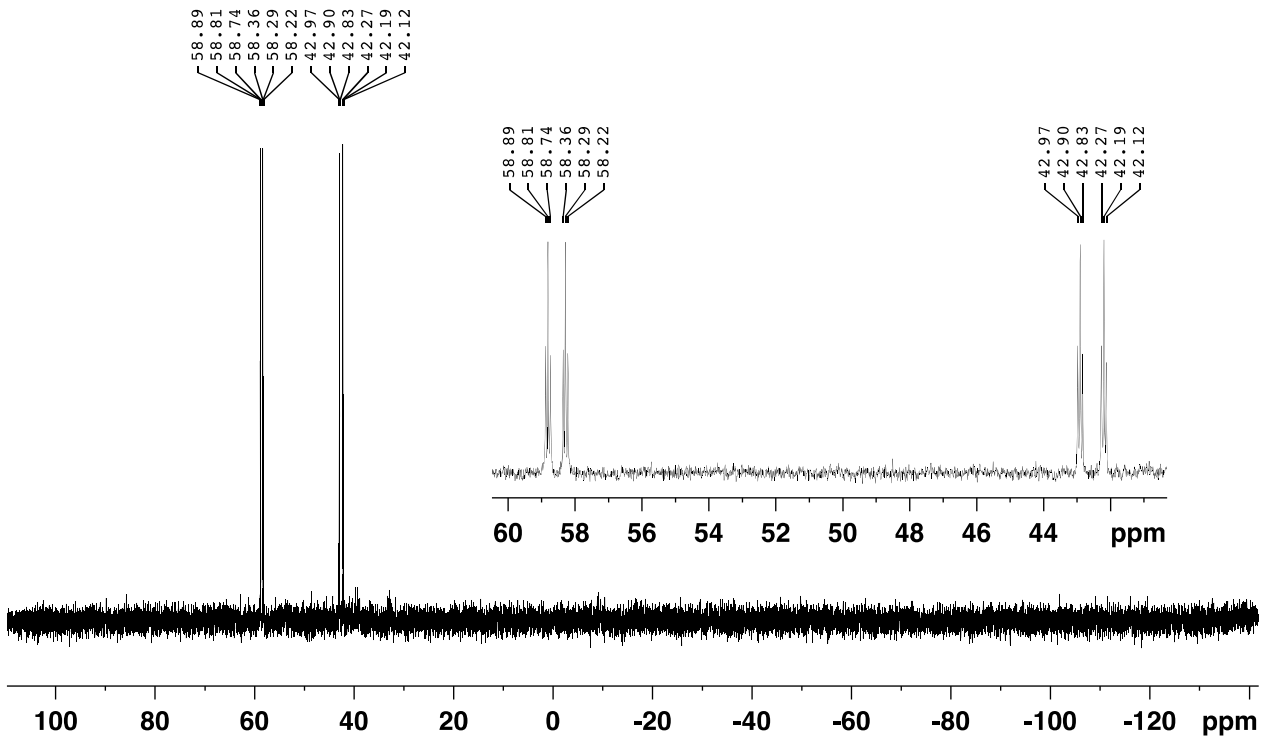

Figure 21. Reaction of **2OAc.OTf** with **11** ^{31}P NMR.

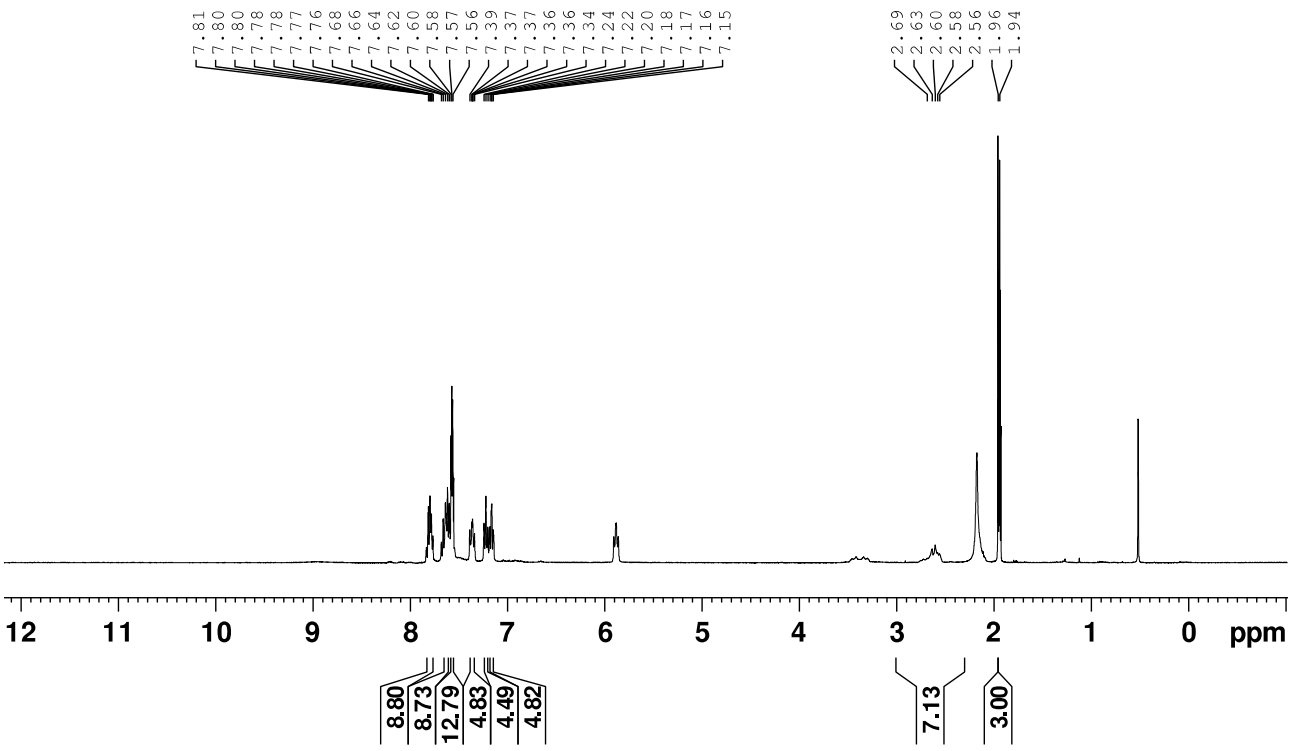

Figure 22. Reaction of **2OAc** with **11** ^{1}H NMR.

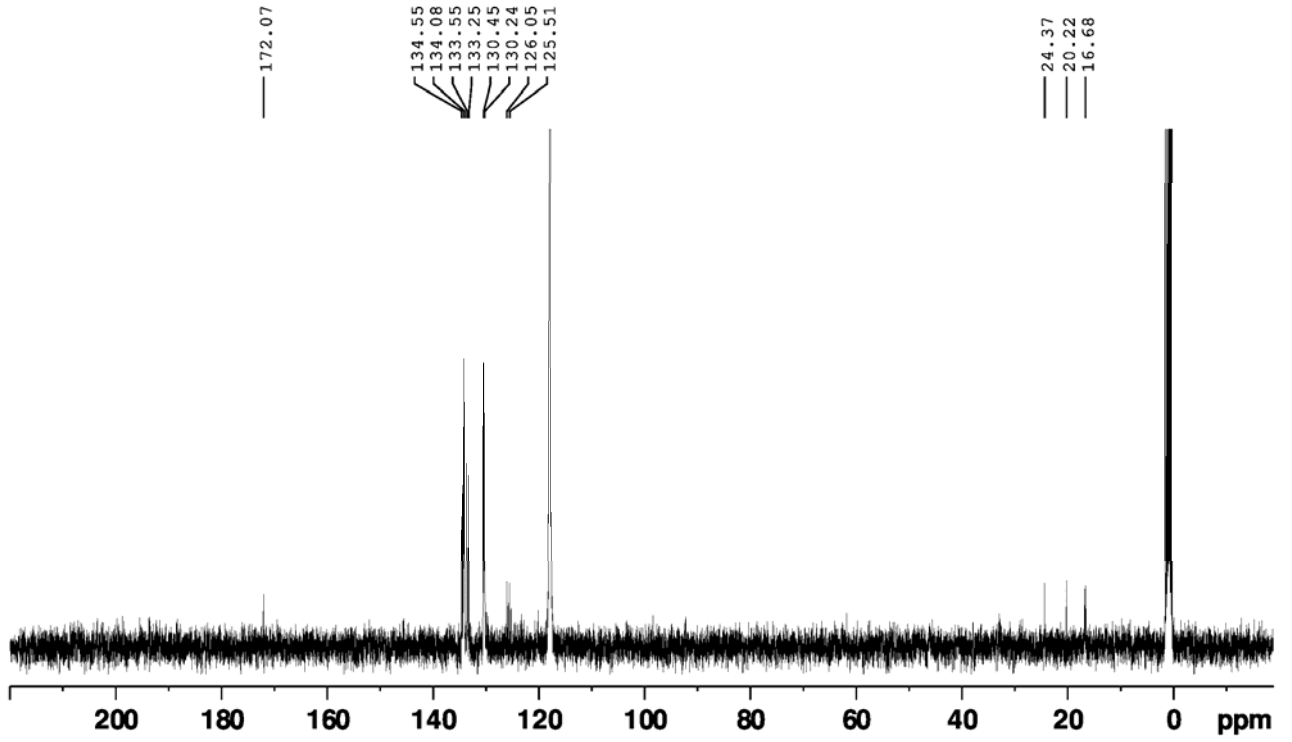

Figure 23. Reaction of **2OAc** with **11** ^{13}C NMR.

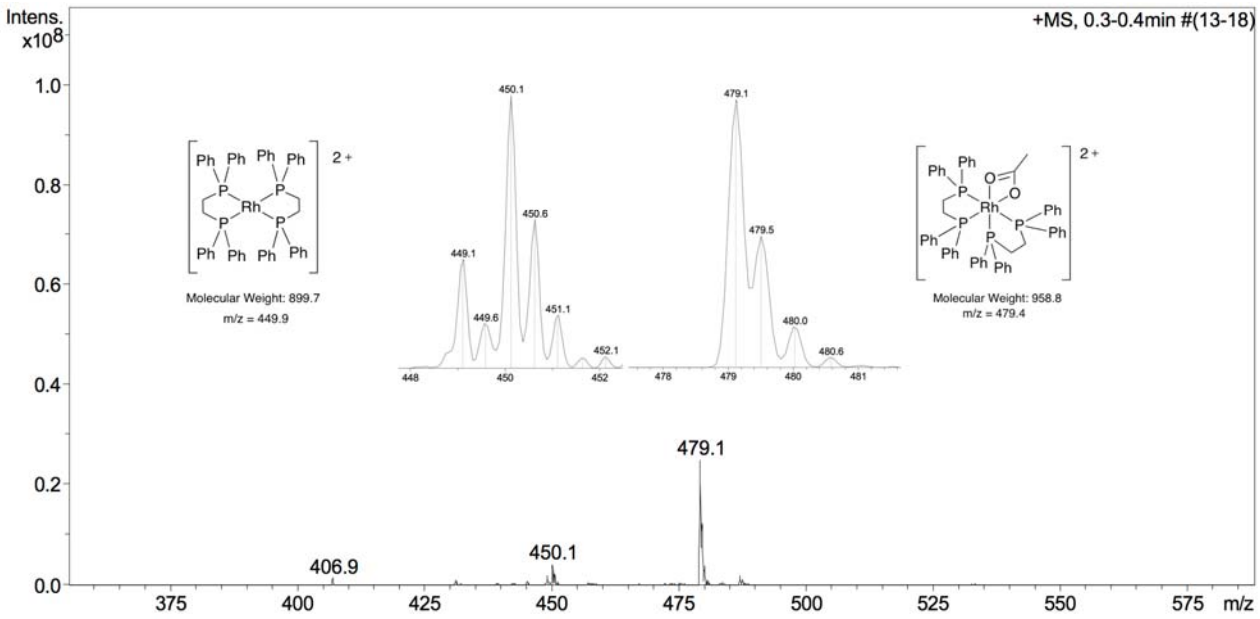

Figure 24. Reaction of **2OAc** with **11** ESI mass spectrum.

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

A solution of **2NMe$_2$** (72 mg, 0.095 mmol) in 5 mL $CDCl_3$ was added drop wise to a solution of **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_2Cl_2) δ (ppm) 40.7 (dt, J= 15, 113 *Hz*), 34.5 (dt, 15, 86 *Hz*). ^{1}H NMR (400 MHz, $CDCl_3$) 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 $[Rh(dppe)_2(DMAP)]^{2+}$.

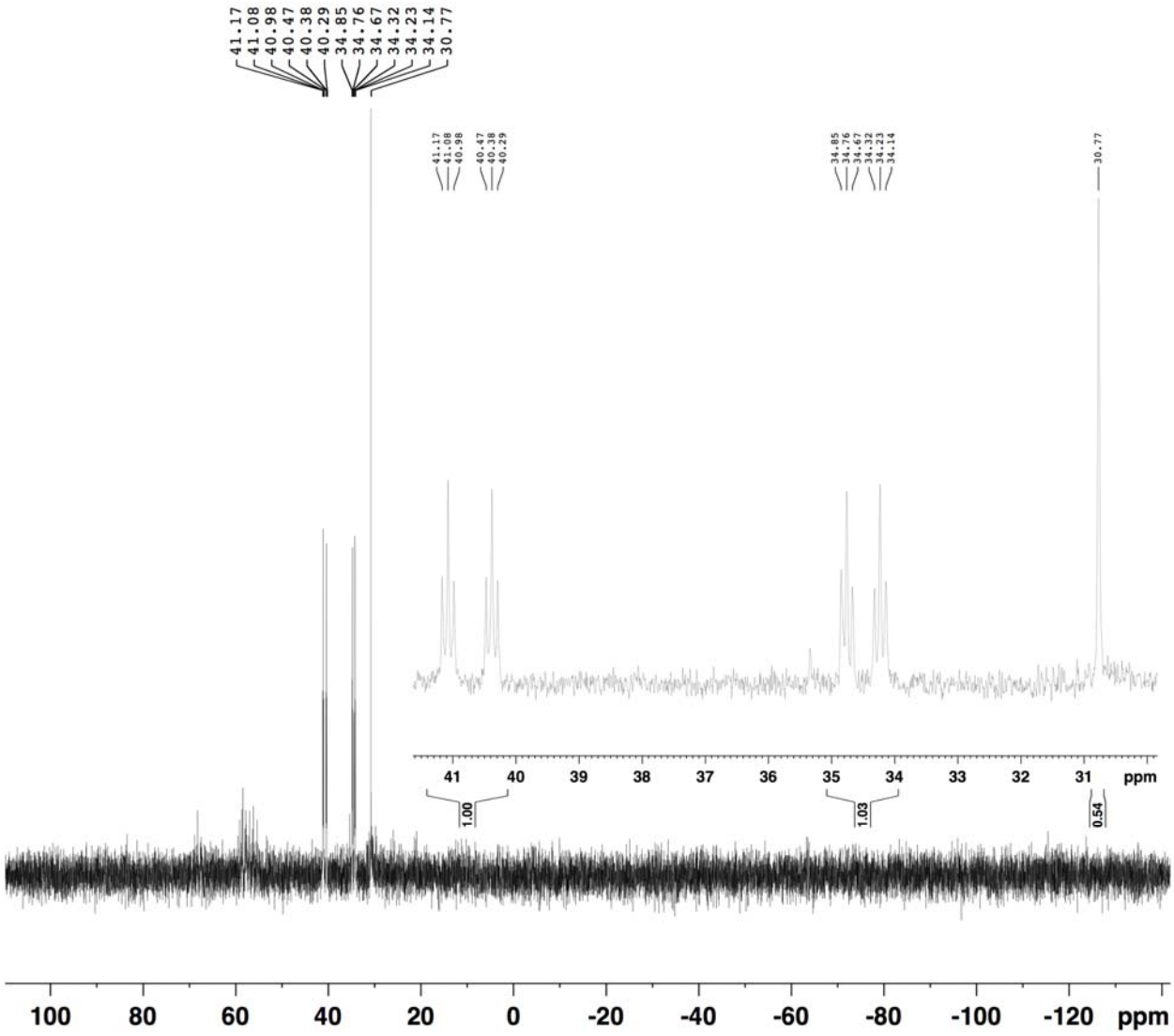

Figure 25. Reaction of **2NMe$_2$** with **11** ^{31}P NMR.

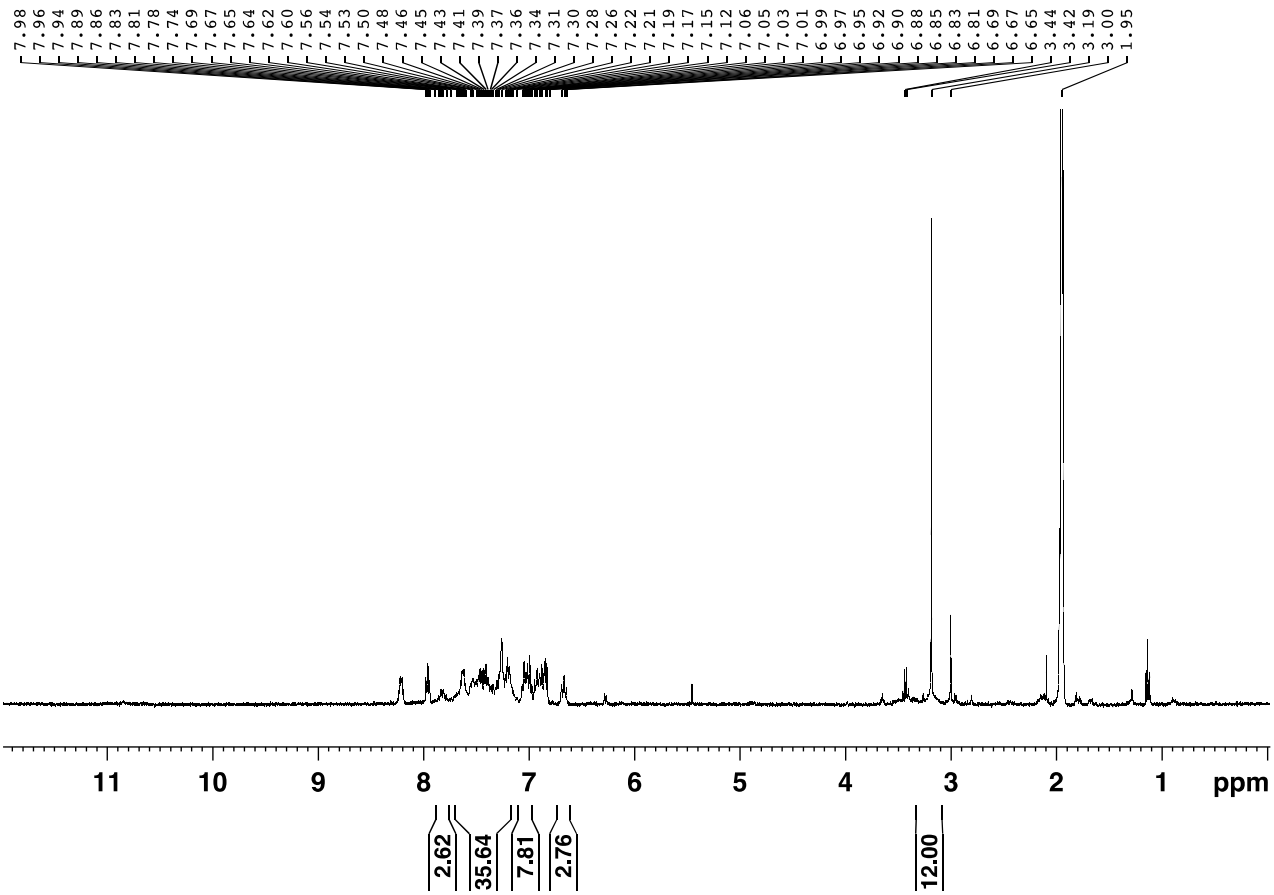

Figure 26. Reaction of **2NMe$_2$** with **11** ^{1}H NMR.

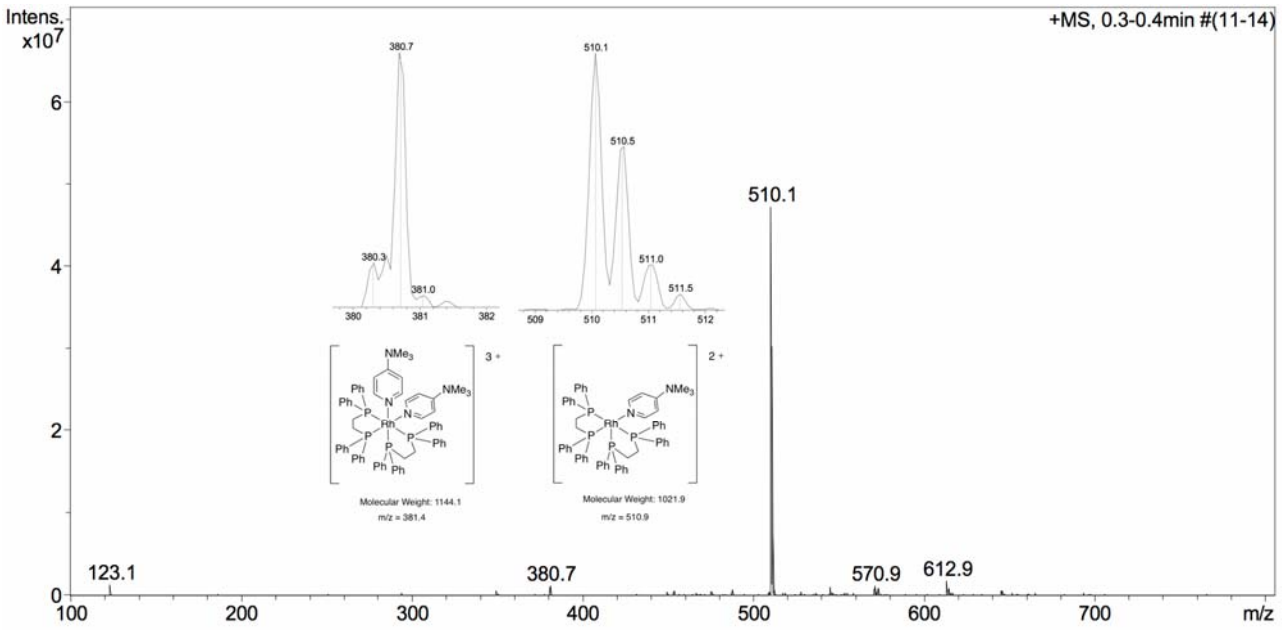

Figure 27. Reaction of **2NMe$_2$** with **11** ESI mass spectrum.

References:

[1] J. P. Collman, C. T. Sears, M. Kubota, A. Davison, E. T. Shawl, J. R. Sowa, R. J. Angelici, *Inorg. Synth.* **1990**, *28*, 92.
[2] J. A. Osborn, G. Wilkinson, J. J. Mrowca, *Inorg. Synth.* **1990**, *28*, 77.
[3] A. J. Kunin, E. J. Nanni, R. Eisenberg, *Inorg. Chem.* **1985**, *24*, 1852.
[4] R. Weiss, J. Seubert, *J. Angew. Chem., Int. Ed.* **1994**, *33*, 891.