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Preparation of benzophenone imine complexes of transition metals

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Dedicated to Piero Zanello.

Abstract

Benzophenone imine $[M(\eta^1\text{-NH=CPh}_2)(CO)_nP_{5-n}]BPh_4$ $[M = Mn, Re; n = 2, 3; P = P(OEt)_3, PPh(OEt)_2, PPh_2OEt, PPh_3]$ complexes were prepared by allowing triflate $M(\kappa^1\text{-OTf})(CO)_nP_{5-n}$ compounds to react with an excess of the imine. Hydride-imine $[MH(\eta^1\text{-NH=CPh}_2)P_4]BPh_4$ (M = Ru, Os), triflate-imine $[Os(\kappa^1\text{-OTf})(\eta^1\text{-NH=CPh}_2)P_4]BPh_4$ and bis(imine) $[Ru(\eta^1\text{-NH=CPh}_2)_2P_4](BPh_4)_2$ $[P = P(OEt)_3]$ derivatives were also prepared. The complexes were characterized spectroscopically (IR, ^1H, ^{31}P, ^{13}C NMR) and a geometry in solution was also established. Hydride-benzophenone imine $[IrHCl(\eta^1\text{-NH=CPh}_2)L(PPh_3)_2]BPh_4$ and $[IrHCl(\eta^1\text{-NH=CPh}_2)L(AsPh_3)_2]BPh_4$ $[L = P(OEt)_3$ and $PPh(OEt)_2]$ complexes were prepared by reacting hydride $IrHCl_2L(PPh_3)_2$ and $IrHCl_2L(AsPh_3)_2$ precursors with an excess of imine. Dihydride $IrH_2(\eta^1\text{-NH=CPh}_2)(PPh_3)_3$ complex was also obtained and a geometry in solution was proposed.

Keywords: Benzophenone imine complexes; Manganese and rhenium; Ruthenium and osmium; Iridium; Phosphite ligands; Synthesis

1. Introduction

Despite the large number of known transition metal complexes containing multidentate imine ligands [1], the monodentate nitrogen-bond imine derivatives are rather rare [2]. This is somewhat surprising, and may be partly due to the weak Lewis basicity of the imine nitrogen atom [1,2]. However, coordination of an imine on a metal fragment would be an important step in its activation toward nucleophilic attack or its hydrogenation reaction to give the amine. Stable complexes can provide models for key intermediate and reaction steps.

We are interested in the coordination chemistry of unsaturated nitrogenous ligands and have extensively studied the chemistry of diazene HN═NH and HN═NR species bonded to a transition metal [3–5]. A series of mono and bis(diazene) complexes of the manganese [3], iron [4] and cobalt [5] triads were therefore prepared and reactivity studies highlighted interesting properties. We have now extended these studies to a species comparable to the diazene group, such as imines (Chart 1), with the aim of determining whether synthesis of imine complexes can be achieved for these metals and, if possible, of comparing results with related diazene derivatives.

The results of these studies, which allow the synthesis of mono- and bis(benzophenone imine) complexes of several transition metals, are reported here.

2. Experimental

2.1. General considerations

All synthetic work was carried out under an inert atmosphere using standard Schlenk techniques or a Vacuum Atmosphere dry-box. Once isolated, the complexes were found to be relatively stable in air, but were stored under an inert atmosphere at −25 °C. All solvents were dried over appropriate drying agents, degassed on a vacuum line and distilled into vacuum-tight storage flasks. The phosphites

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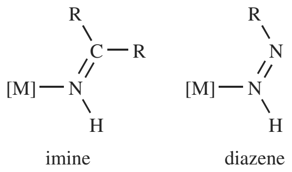


Chart 1.

$PPh(OEt)_2$ and PPh_2OEt were prepared by the method of Rabinowitz and Pellon [6], whereas $P(OEt)_3$ was an Aldrich product, purified by distillation under nitrogen. $Mn_2(CO)_{10}$ (Aldrich), $Re_2(CO)_{10}$, $RuCl_3 \cdot 3H_2O$, $(NH_4)_2OsCl_6$ and $IrCl_3 \cdot 3H_2O$ (Pressure Chem., USA) salts were used without any further purification. Other reagents were purchased from commercial sources (Aldrich, Fluka) in the highest available purity and used as received. Infrared spectra were recorded on Nicolet Magna 750 or Perkin–Elmer Spectrum One FT-IR spectrophotometers. NMR spectra (^1H, ^{13}C, ^{31}P) were obtained on Bruker AC200 or AVANCE 300 spectrometers at temperatures varying between −90 and +30 °C, unless otherwise noted. ^1H and ^{13}C spectra are referred to internal tetramethylsilane, while $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. The COSY, HMQC and HMBC NMR experiments were performed using their standard programs. The SwaN-MR software package [7] was used to treat NMR data. The conductivities of 10^{-3} M solutions of the complexes in CH_3NO_2 at 25 °C were measured with a Radiometer CDM 83 instrument. Elemental analyses were determinated in the Microanalytical Laboratory of the Dipartimento di Scienze Farmaceutiche of the University of Padova (Italy).

2.2. Synthesis of complexes

The hydride complexes $MH(CO)_3P_2$, $MH(CO)_2P_3$ [M = Mn, Re; P = $P(OEt)_3$, $PPh(OEt)_2$, PPh_2OEt, PPh_3], MH_2P_4 [M=Ru,Os;P=$P(OEt)_3$], $IrHCl_2L(PPh_3)_2$, $IrHCl_2L(AsPh_3)_2$ [L=$P(OEt)_3$ and $PPh(OEt)_2$] and $IrH_2Cl(PPh_3)_3$ were prepared following the reported methods [4d,5a,8–10].

2.2.1. $[M(\eta^1\text{-}NH{=}CPh_2)(CO)nP_{5-n}]BPh_4$ (1–4) [M=Mn (1, 2), Re (3, 4); P=$P(OEt)_3$ (a), $PPh(OEt)_2$ (b), PPh_2OEt (c), PPh_3 (d); n = 3 (1, 3), 2 (2, 4)]

An equimolar amount of triflic acid (HOTf) (0.2 mmol, 18 μL) was added to a solution of the appropriate hydride $MH(CO)_nP_{5-n}$ (0.2 mmol) in 7 mL of toluene cooled to −196 °C. The reaction mixture was brought to room temperature, stirred for 1 h and then an excess of benzophenone imine ($Ph_2C{=}NH$, 1.6 mmol, 27 μL) was added. The resulting solution was stirred for about 20 h and then the solvent was removed under reduced pressure to give an oil which was triturated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.45 mmol, 154 mg). A yellow or white solid slowly separated out from the resulting solution, which was filtered and crystallized from CH_2Cl_2 and ethanol; yield from 61% to 83% [126 mg, 61% (**1b**), 164 mg, 68% (**2b**), 143 mg, 65% (**3a**), 168 mg, 72% (**3b**), 195 mg, 79% (**3c**), 215 mg, 83% (**3d**), 195 mg, 73% (**4b**)]. *Anal.* Calc. for $C_{60}H_{61}BMnNO_7P_2$ (**1b**) (1035.84): C, 69.57; H, 5.94; N, 1.35. $\Lambda_M = 52.2\ \Omega^{-1}\ mol^{-1}\ cm^2$. Found: C, 69.72; H, 5.90; N, 1.28%. *Anal.* Calc. for $C_{69}H_{76}BMnNO_8P_3$ (**2b**) (1206.03): C, 68.72; H, 6.35; N, 1.16. $\Lambda_M = 54.5\ \Omega^{-1}\ mol^{-1}\ cm^2$. Found: C, 68.58; H, 6.30; N, 1.09%. *Anal.* Calc. for $C_{52}H_{61}BNO_9P_2Re$ (**3a**) (1103.01): C, 56.62; H, 5.57; N, 1.27. Found: C, 56.78; H, 5.62; N, 1.20%. $\Lambda_M = 54.7\ \Omega^{-1}\ mol^{-1}\ cm^2$. *Anal.* Calc. for $C_{60}H_{61}BNO_7P_2Re$ (**3b**) (1167.10): C, 61.75; H, 5.27; N, 1.20. Found: C, 61.54; H, 5.39; N, 1.12%. $\Lambda_M = 51.6\ \Omega^{-1}\ mol^{-1}\ cm^2$. *Anal.* Calc. for $C_{68}H_{61}BNO_5P_2Re$ (**3c**) (1231.19): C, 66.34; H, 4.99; N, 1.14. Found: C, 66.45; H, 5.12; N, 1.04%. $\Lambda_M = 53.9\ \Omega^{-1}\ mol^{-1}\ cm^2$. *Anal.* Calc. for $C_{76}H_{61}BNO_3P_2Re$ (**3d**) (1295.28): C, 70.47; H, 4.75; N, 1.08. $\Lambda_M = 54.7\ \Omega^{-1}\ mol^{-1}\ cm^2$. Found: C, 70.28; H, 4.63; N, 1.16%. *Anal.* Calc. for $C_{69}H_{76}BNO_8P_3Re$ (**4b**) (1337.29): C, 61.97; H, 5.73; N, 1.05. Found: C, 61.74; H, 5.65; N, 0.96%. $\Lambda_M = 55.8\ \Omega^{-1}\ mol^{-1}\ cm^2$.

2.2.2. $[MH(\eta^1\text{-}NH{=}CPh_2)\{P(OEt)_3\}_4]BPh_4$ (5, 6) [M=Ru (5), Os (6)]

An equimolar amount of triflic acid (HOTf) (0.2 mmol, 18 μL) was added to a solution of the appropriate dihydride $MH_2[P(OEt)_3]_4$ (0.2 mmol) in 10 mL of toluene cooled to −196 °C. The solution was allowed to reach room temperature and then stirred for 1 h. An excess of benzophenone imine $Ph_2C{=}NH$ (1.6 mmol, 0.27 mL) was added and the reaction mixture stirred for about 20 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol containing an excess of $NaBPh_4$ (0.5 mmol, 171 mg). A white solid slowly separated out from the resulting solution which was filtered and crystallized from CH_2Cl_2 and ethanol [190 mg, 75% (**5**), 214 mg, 79% (**6**)]. *Anal.* Calc. for $C_{61}H_{92}BNO_{12}P_4Ru$ (**5**) (1267.17): C, 57.82; H, 7.32; N, 1.11. Found: C, 57.67; H, 7.43; N, 1.17%. $\Lambda_M = 50.4\ \Omega^{-1}\ mol^{-1}\ cm^2$. *Anal.* Calc. for $C_{61}H_{92}BNO_{12}OsP_4$ (**6**) (1356.30): C, 54.02; H, 6.84; N, 1.03. Found: C, 54.19; H, 6.76; N, 1.08%. $\Lambda_M = 54.9\ \Omega^{-1}\ mol^{-1}\ cm^2$.

2.2.3. $[Ru(\eta^1\text{-}NH{=}CPh_2)_2\{P(OEt)_3\}_4](BPh_4)_2$ (7)

Triflic acid (0.2 mmol, 18 μL) was added to a solution of $RuH_2[P(OEt)_3]_4$ (0.153 g, 0.2 mmol) in 10 mL of toluene cooled to −196 °C. The solution was brought to 0 °C, stirred for 2 h and then cooled again to −196 °C. Triflic acid was added (0.2 mmol, 18 μL) and the reaction mixture, brought to room temperature, stirred for about 90 min. An excess of benzophenone imine $Ph_2C{=}NH$ (2.0 mmol, 0.34 mL) was added and the reaction mixture stirred for about 20 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.8 mmol, 0.274 g). A white solid separated out which was filtered and crystallized from CH_2Cl_2 and ethanol (265 mg, 75%). *Anal.* Calc. for $C_{98}H_{122}B_2N_2O_{12}P_4Ru$ (1766.63): C, 66.63; H, 6.96; N, 1.59. $\Lambda_M = 125\ \Omega^{-1}\ \text{mol}^{-1}$. Found: C, 66.49; H, 7.05; N, 1.49%.

2.2.4. $[Os(\kappa^1\text{-}OTf)(\eta^1\text{-}NH{=}CPh_2)\{P(OEt)_3\}_4]BPh_4$ (**8**)

Methyltriflate (CH_3OTf, 0.18 mmol, 20 μL) was added to a solution of the dihydride $OsH_2[P(OEt)_3]_4$ (0.18 mmol, 154 mg) in toluene (7 mL) cooled to −196 °C. The reaction mixture was brought to room temperature, stirred for 1 h and then cooled again to −196 °C. Triflic acid (0.18 mmol, 16 μL) was added and the reaction mixture, brought to room temperature, stirred for about 90 min. An excess of benzophenone imine $Ph_2C{=}NH$ (1.8 mmol, 0.30 mL) was added and the resulting solution stirred for about 20 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.72 mmol, 0.25 g). A white solid slowly separated out, which was filtered and crystallized from CH_2Cl_2 and ethanol (168 mg, 62%). *Anal.* Calc. for $C_{62}H_{91}BF_3NO_{15}OsP_4S$ (1504.36): C, 49.50; H, 6.10; N, 0.93. Found: C, 49.34; H, 6.17; N, 0.99%. $\Lambda_M = 56.7\ \Omega^{-1}\ \text{mol}^{-1}$.

2.2.5. $IrHCl(\eta^1\text{-}NH{=}CPh_2)L(PPh_3)_2$ (**9**) [$L{=}P(OEt)_3$ (**a**), $PPh(OEt)_2$ (**b**)]

A slight excess of benzophenone imine $Ph_2C{=}NH$ (0.13 mmol, 22 μL) was added to a solution of the appropriate hydride $IrHCl_2L(PPh_3)_2$ (0.12 mmol) in 7 mL of CH_2Cl_2 and the solution stirred for 20 h. The solvent was removed under reduced pressure giving an oil which was triturated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.24 mmol, 82 mg). A yellow solid slowly separated out which was filtered and crystallized from CH_2Cl_2 and ethanol [112 mg, 66% (**9a**), 122 mg, 70% (**9b**)]. *Anal.* Calc. for $C_{79}H_{77}BClIrNO_3P_3$ (**9a**) (1419.89): C, 66.83; H, 5.47; Cl, 2.50; N, 0.99. Found: C, 66.65; H, 5.61; Cl, 2.36; N, 1.06%. *Anal.* Calc. for $C_{83}H_{77}BClIrNO_2P_3$ (**9b**) (1451.93): C, 68.66; H, 5.35; Cl, 2.44; N, 0.96. Found: C, 68.64; H, 5.46; Cl, 2.31; N, 0.89%.

2.2.6. $IrHCl(\eta^1\text{-}NH{=}CPh_2)L\ (AsPh_3)_2$ (**10**) [$L{=}P(OEt)_3$ (**a**), $PPh(OEt)_2$ (**b**)]

These complexes were prepared exactly like the related compounds **9** using a reaction time of 24 h [132 mg, 73% (**10a**), 142 mg, 77% (**10b**)]. *Anal.* Calc. for $C_{79}H_{77}As_2BClIrNO_3P$ (**10a**) (1507.78): C, 62.93; H, 5.15; Cl, 2.35; N, 0.93. Found: C, 62.74; H, 5.21; Cl, 2.40; N, 1.02%. *Anal.* Calc. for $C_{83}H_{77}As_2BClIrNO_2P$ (**10b**) (1539.83): C, 64.74; H, 5.04; Cl, 2.30; N, 0.91. Found: C, 64.79; H, 5.13; Cl, 2.35; N, 0.87%.

2.2.7. $[IrH_2(\eta^1\text{-}NH{=}CPh_2)\ (PPh_3)_3]BPh_4$ (**11**)

A slight excess of $Ph_2C{=}NH$ (0.13 mmol, 22 μL) was added to a solution of the hydride $IrH_2Cl(PPh_3)_3$ (0.12 mmol, 122 mg) in CH_2Cl_2 (7 mL) cooled to −196 °C. The reaction mixture was brought to room temperature, stirred for 20 h, and then the solvent removed under reduced pressure. The oil obtained was triturated with ethanol containing an excess of $NaBPh_4$ (0.24 mmol, 82 mg). A yellow solid slowly separated out from the solution, which was filtered and crystallized from CH_2Cl_2 and ethanol (123 mg, 69%). *Anal.* Calc. for $C_{91}H_{78}BIrNP_3$ (1481.58): C, 73.77; H, 5.31; N, 0.95. Found: C, 73.61; H, 5.19; N, 0.90%. $\Lambda_M = 53.0\ \Omega^{-1}\ \text{mol}^{-1}$.

2.2.8. $[Re\{(CH_3)_2CHNH_2\}(CO)_2\{PPh(OEt)_2\}_3]\ BPh_4$ (**12**)

An equimolar amount of triflic acid (HOTf) (0.15 mmol, 13 μL) was added to a solution of $ReH(CO)_2[PPh(OEt)_2]_3$ (0.15 mmol, 125 mg) in toluene (10 mL) cooled to −196 °C. The reaction mixture was brought to room temperature, stirred for about 1 h and then an excess of the amine $(CH_3)_2CHNH_2$ (1.2 mmol, 102 μL) was added. The solution was stirred for 20 h and then the solvent removed under reduced pressure. The oil obtained was triturated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.3 mmol, 103 mg). A white solid separated out which was filtered and crystallized from CH_2Cl_2 and ethanol (140 mg, 77%). *Anal.* Calc. for $C_{59}H_{74}BNO_8P_3Re$ (1215.17): C, 58.32; H, 6.14; N, 1.15. Found: C, 58.45; H, 6.25; N, 1.06%. $\Lambda_M = 56.9\ \Omega^{-1}\ \text{mol}^{-1}$.

2.2.9. $[RuH(RNH_2)\{P(OEt)_3\}_4]\ BPh_4$ (**13, 14**) [$R{=}Ph_2CH$ (**13**), $(CH_3)_2CH$ (**14**)]

Triflic acid (0.13 mmol, 12 μL) was added to a solution of the dihydride $RuH_2[P(OEt)_3]_4$ (0.13 mmol, 100 mg) in toluene (7 mL) cooled to −196 °C and the reaction mixture, brought to 0 °C, was stirred for 1 h. An excess of the appropriate amine (1 mmol) was added and the reaction mixture stirred for 20 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.40 mmol, 137 mg). A white solid slowly separated out which was filtered and crystallized from CH_2Cl_2 and ethanol; yield between 65% and 78% [107 mg, 65% (**13**), 116 mg, 78% (**14**)]. *Anal.* Calc. for $C_{61}H_{94}BNO_{12}P_4Ru$ (**13**) (1269.19): C, 57.73; H, 7.46; N, 1.10. Found: C, 57.59; H, 7.40; N, 0.96%. $\Lambda_M = 51.7\ \Omega^{-1}\ \text{mol}^{-1}$. *Anal.* Calc. for $C_{51}H_{90}BNO_{12}P_4Ru$ (**14**) (1145.05): C, 53.50; H, 7.92; N, 1.22. Found: C, 53.63; H, 7.98; N, 1.16%. $\Lambda_M = 54.4\ \Omega^{-1}\ \text{mol}^{-1}$.

2.2.10. Oxidation reactions

The oxidation reactions were carried out at room and low temperature (−30 °C) in CH_2Cl_2, using $Pb(OAc)_4$ as a reagent. In a typical experiment, the solid sample of amine complex **12**–**14** (0.2 mmol) was placed in a three-necked 25-mL flask fitted with a solid-addition sidearm containing $Pb(OAc)_4$ (0.2 mmol, 89 mg). The apparatus was evacuated, CH_2Cl_2 (10 mL) was added, the solution was cooled to −30 °C and $Pb(OAc)_4$ was added portion-wise over 10–20 min to the cold stirring solution. The reaction mixture was then allowed to warm to 0 °C, stirred for 20 min and then the solvent was removed under reduced pressure at 0 °C. The oil obtained was treated at the same temperature with ethanol (2 mL) obtaining a white solid, which was filtered and dried under vacuum.

3. Results and discussion

3.1. Manganese, rhenium, ruthenium and osmium complexes

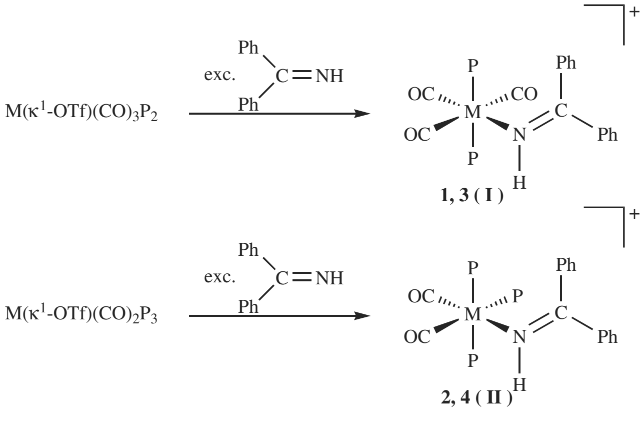
Imine complexes of manganese and rhenium of the $[M(\eta^1\text{-NH=CPh}_2)(CO)_nP_{5-n}]BPh_4$ (**1**–**4**) types were synthesized by reacting triflate complexes $M(\kappa^1\text{-OTf})(CO)_n\text{-}P_{5-n}$ with an excess of free imine, as shown in Scheme 1.

Triflates $M(\kappa^1\text{-OTf})(CO)_nP_{5-n}$ were generated in situ by reacting hydride $MH(CO)_nP_{5-n}$ species with 1 eq of triflic acid at low temperature, as previously reported [8,9]. Substitution of the labile triflate ligand with the *N*-protio imine $Ph_2C{=}NH$ gives the final complexes **1**–**4**, which were separated as BPh_4 salts and characterized.

Substitution of the labile triflate ligand also allowed us to prepare benzophenone imine complexes of ruthenium and osmium, as shown in Scheme 2.

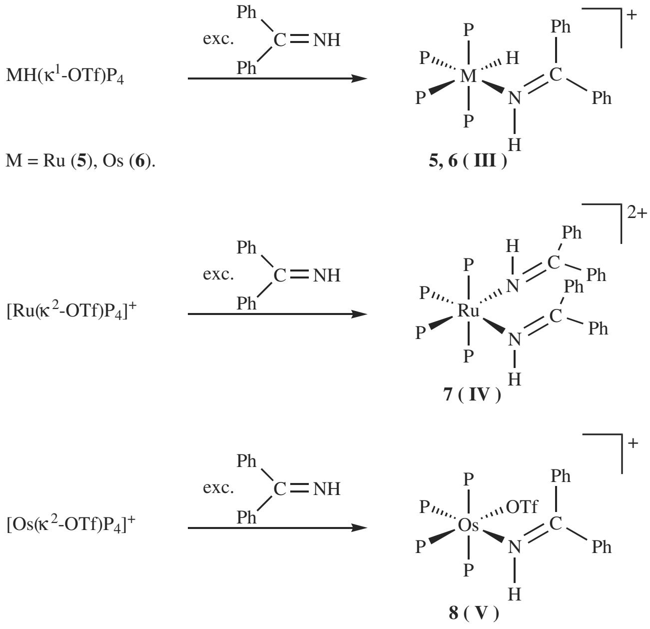
Thus, hydride-imine $[MH(\eta^1\text{-NH=CPh}_2)P_4]^+$ (**5**, **6**) complexes of both ruthenium and osmium were obtained from hydride-triflate $MH(\kappa^1\text{-OTf})P_4$ precursors [11]. Instead, bis(imine) $[M(\eta^1\text{-NH=CPh}_2)_2P_4]^{2+}$ derivatives were prepared only in the case of ruthenium, because, with osmium, the reaction of the κ^2-triflate $[M(\kappa^2\text{-OTf})P_4]^+$ cation with an excess of imine always gave imine-triflate $[Os(\kappa^1\text{-OTf})(\eta^1\text{-NH=CPh}_2)P_4]^+$ complexes **8**.

The easy synthesis of benzophenone imine complexes **1**–**8** also prompted us to prepare complexes containing *N*-substituted imine R1(R2)C=N(R). We therefore reacted the triflate $M(\kappa^1\text{-OTf})(CO)_nP_{5-n}$ (M = Mn, Re) and $MH(\kappa^1\text{-OTf})P_4$ (M = Ru, Os) precursors with the *N*-methyl $PhC(H){=}NCH_3$ imine in various conditions, but no imine complexes were obtained (Scheme 3).



M = Mn (**1**,**2**), Re (**3**, **4**); P = $P(OEt)_3$, $PPh(OEt)_2$, PPh_2OEt

Scheme 1.



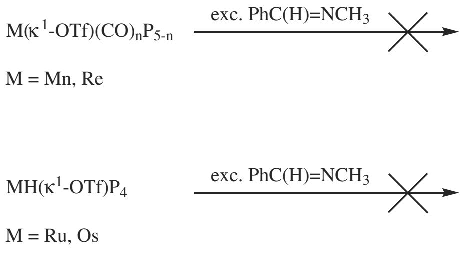
P = $P(OEt)_3$

Scheme 2.

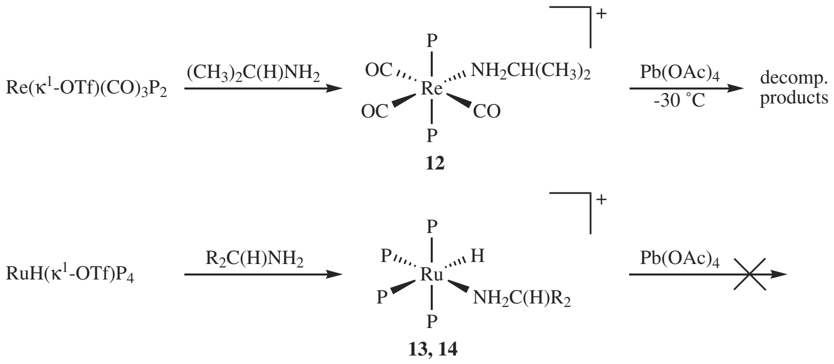
At room temperature, substitution of the triflate does not take place, whereas refluxing conditions caused some decomposition, giving intractable mixtures of products. In contrast with the *N*-protio $Ph_2C{=}NH$ imine, the *N*-methyl imine does not yield the corresponding imine $[M]{-}N(CH_3){=}C(H)Ph$ derivatives, probably owing to steric hindrance of the *N*-methyl group, which makes the $PhC(H){=}NCH_3$ imine a poor coordinating ligand.

Protio-imine complexes of transition metals have previously been prepared following methods not applying substitution of a labile ligand. Taube et al. [2a] prepared an imine complex from the reaction of coordinate NH_3 with acetone, and Templeton et al. [2d] prepared from the reduction of coordinate acetonitrile. Instead, Gladysz et al. [2e] prepared a rhenium imine derivative from the reaction of a coordinate nitrile, first with Grignard's reagent and then with triflic acid.

We also attempted to prepare imine complexes following a new method, involving oxidation of the coordinate amine. For this purpose, we prepared some amine complexes of rhenium and ruthenium and studied their oxidation reactions with $Pb(OAc)_4$ [12] (Scheme 4).



Scheme 3.



R = CH_3 (**13**), Ph (**14**).

Scheme 4.

Unfortunately, results show that this method was not suitable for our complexes, and no imine complexes were obtained using $Pb(OAc)_4$ as an oxidant. Ruthenium complexes **13**, **14** do not react with $Pb(OAc)_4$ in any conditions, and the starting amine complexes were recovered unchanged after several hours of reaction. Other oxidizing reagents such as MnO_2, PbO_2 and H_2O_2 were used with complexes **13**, **14**, but here too no reactions were observed.

However, the rhenium $[Re\{(CH_3)_2C(H)NH_2\}(CO)_2P_3]^+$ cation **12** reacted with an excess of $Pb(OAc)_4$ at low temperature (−30 °C) to give a yellow solution, from which an oily product was isolated, although its ^1H NMR spectra did not indicate the presence of any imine complex. Therefore, it seems that only by substitution of a labile ligand can the preparation of benzophenone imine complexes take place for the phosphite-containing Mn, Re, Ru and Os metal derivatives.

Imine complexes **1**–**8** are yellow or white solids, stable in air and in solution of polar organic solvents, in which they behave as 1:1 electrolytes, except for bis(imine) $[Ru(\eta^1\text{-}NH{=}CPh_2)_2P_4](BPh_4)_2$ complex **7**, which behaves like a 2:1 electrolyte [13]. Analytical and spectroscopic data (Table 1) support the proposed formulation.

The IR spectra of tricarbonyl $[M(\eta^1\text{-NH}{=}CPh_2)(CO)_3P_2]BPh_4$ complexes (**1**, **3**) of both Mn and Re show three bands in the ν_{CO} region, one of medium intensity and two strong, suggesting a *mer* arrangement of the three carbonyl ligands [14]. The spectra also show a medium-intensity band at 3226–3204 cm^{-1} attributed to the ν_{NH} of the imine ligand.

However, the presence of the $Ph_2C{=}NH$ group in the complexes was confirmed by the ^1H NMR spectra, with a slightly broad signal at 9.55–8.80 ppm due to the NH proton resonances of the imine ligand. This signal, in an HMBC experiment for compound **3b**, is also correlated with a triplet at 183.2 ppm ($J_{CP} = 2$ Hz), attributed to the C=NH carbon resonance of the imine, in agreement with the proposed formulation.

In the temperature range between +20 and −80 °C, the ^{31}P NMR spectra of $[Re(\eta^1\text{-NH}{=}CPh_2)(CO)_3P_2]BPh_4$ complexes **3** are sharp singlets, fitting the magnetic equivalence of the two phosphite ligands. The ^{31}P NMR spectra of the related manganese complexes **1** are broad at room temperature, but resolve into a sharp singlet at −80 °C, again fitting the magnetic equivalence of the two phosphite ligands. On the basis of these data, a *mer-trans* geometry (**I**, Scheme 1) may be proposed for our tricarbonyl derivatives.

The IR spectra of dicarbonyl $[M(\eta^1\text{-NH}{=}CPh_2)(CO)_2P_3]BPh_4$ (**2**, **4**) complexes show two strong absorptions in the ν_{CO} region at 1983–1902 cm^{-1}, suggesting a *cis* arrangement of the two carbonyl ligands. However, these two CO groups are not magnetically equivalent since the ^{13}C NMR spectra of the complexes show two well-separated multiplets at 223.4 and 215.8 ppm for **2b** and at 196.4 and 192.9 for **4b**. The $^{31}P\{^1H\}$ NMR spectra of the dicarbonyl derivatives of manganese **2b** change as the temperature is lowered and, at −70 °C, appear as an A_2B multiplet simulable with the parameters reported in Table 1. In the temperature range between +20 and −80 °C, also the $^{31}P\{^1H\}$ NMR spectra of the related rhenium dicarbonyl complex **4b** are AB_2 multiplets, indicating the magnetic equivalence of two phosphites, unlike the third. On the basis of these data, a *mer-cis* geometry of type **II** (Scheme 1) may be proposed for the dicarbonyl imine derivatives.

Comparisons with previous results from our laboratory [3] highlight the interesting ability of the mixed-ligand $M(CO)_nP_{5-n}$ fragment (M = Mn, Re) with phosphite and carbonyl to coordinate unsaturated nitrogenous ligands. In fact, 1,2-diazene $[M(\eta^1\text{-NH}{=}NH)(CO)_nP_{5-n}]BPh_4$ and aryldiazene $[M(\eta^1\text{-NH}{=}NAr)(CO)_nP_{5-n}]BPh_4$ complexes were previously prepared for both manganese [3a,3d] and rhenium [3b,3e] and are stable and isolable like the benzophenone imine derivatives **1**–**4** reported here. In addition, the simplest imine ligand, $CH_2{=}NH$, was stabilized for the first time, using right the rhenium fragment $Re(CO)_np_{5-n}$ to give the related [Re]-η^1-$NH{=}CH_2$ complex [15]. Therefore, the ability of $Re(CO)_nP_{5-n}$ fragments to coordinate an imine group is confirmed when the benzophenone imine ligand is used.

The IR spectra of the imine $[MH(\eta^1\text{-NH}{=}CPh_2)P_4]BPh_4$ complexes of ruthenium and osmium **5** and **6** show

Table 1
IR and NMR data for all complexes

	Compound	IR[a] (cm^{-1})	Assgnt	^1H NMR[b,c] δ (J, Hz)	Assgnt	Spin system	$^{31}P\{^1H\}$ NMR[b,d] δ (J, Hz)
1b	$[Mn(\eta^1\text{-}NH{=}CPh_2)(CO)_3\{PPh(OEt)_2\}_2]BPh_4$	3223 m	ν_H	9.05 s	=NH	A_2	158 br
		2065 m	ν_O	4.00 m	CH_2	A_2[e]	160.4 s
		1986 s		1.23 t	CH_3		
		1940 s					
2b	$[Mn(\eta^1\text{-}NH{=}CPh_2)(CO)_2\{PPh(OEt)_2\}_3]BPh_4$[f]	3226 m	ν_{NH}	9.93 d	=NH	A_2B[e]	δ_A 190.4
		1968 s	ν_{CO}	$J_{PH} = 10$			δ_B 177.6
		1902 s		3.77 m	CH_2		$J_{AB} = 75.0$
				3.49 m			
				1.18 t	CH_3		
				1.09 t			
3a	$[Re(\eta^1\text{-}NH{=}CPh_2)(CO)_3\{P(OEt)_3\}_2]BPh_4$	3215 m	ν_{NH}	9.55 s	=NH	A_2	110.5 s
		2072 m	ν_{CO}	4.05 m	CH_2		
		1971 s		1.32 t	CH_3		
		1929 s					
3b	$[Re(\eta^1\text{-}NH{=}CPh_2)(CO)_3\{PPh(OEt)_2\}_2]BPh_4$[g]	3204 m	ν_{NH}	9.28 s, br	=NH	A_2	133.2 s
		2065 m	ν_{CO}	4.04 m	CH_2		
		1980 s		1.38 t	CH_3		
		1940 s					
3c	$[Re(\eta^1\text{-}NH{=}CPh_2)(CO)_3(PPh_2OEt)_2]BPh_4$	3215 w	ν_{NH}	9.18 s	=NH	A_2	107.5 s
		2056 m	ν_{CO}	3.54 m	CH_2		
		1960 s		1.18 t	CH_3		
		1934 s					
3d	$[Re(\eta^1\text{-}NH{=}CPh_2)(CO)_3(PPh_3)_2]BPh_4$	3211 w	ν_{NH}	8.80 s, br	=NH	A_2	13.8 s
		2067 m	nu^{CO}				
		1966 s					
		1914 s					
4b	$[Re(\eta^1\text{-}NH{=}CPh_2)(CO)_2\{PPh(OEt)_2\}_3]BPh_4$[h]	3240 m	ν_{NH}	9.95 d, br	=NH	AB_2	δ_A 135.9
		1983 s	ν_{CO}	$J_{PH} = 8$			δ_B 134.1
		1902 s		4.00–3.55 m	CH_2		$J_{AB} = 33.5$
				1.33 t	CH_3		
				1.21 t			
				1.15 t			
5	$[RuH(\eta^1\text{-}NH{=}CPh_2)\{P(OEt)_3\}_4]BPh_4$	3285 m	ν_{NH}	10.40 d, br	=NH	AB_2C	δ_A 148.6
		1911 w	ν_{RuH}	$J_{PH} = 6.8$			δ_B 142.9
				4.25-3.70 m	CH_2		δ_C 136.8
				1.32 t	CH_3		$J_{AB} = 63.5$
				1.21 t			$J_{AC} = 40.9$
				1.13 t			$J_{BC} = 44.1$
				−7.11 to −8.18 m	RuH		
6	$[OsH(\eta^1\text{-}NH{=}CPh_2)\{P(OEt)_3\}_4]BPh_4$	3219 m	ν_{NH}	10.87 d, br	=NH	A_2BC	δ_A 104.3
		1987 w	ν_{OsH}	4.25–3.00 m	CH_2		δ_B 101.6
				1.27 t	CH_3		δ_C 96.4
				1.16 t			$J_{AB} = 32.9$
				1.12 t			$J_{AC} = 44.2$
				−8.22 to −9.07 m	OsH		$J_{BC} = 28.8$
7	$[Ru(\eta^1\text{-}NH{=}CPh_2)_2\{P(OEt)_3\}_4](BPh_4)_2$	3223 m	ν_{NH}	10.46 s, br	=NH	ABC_2	δ_A 129.5
				4.08 m	CH_2		δ_B 129.2
				1.27 t	CH_3		δ_C 119.6
				1.25 t			$J_{AB} = 37.7$
							$J_{AC} = 59.1$
							$J_{BC} = 60.8$
8	$[Os(\kappa^1\text{-}OTf)(\eta^1\text{-}NH{=}CPh_2)\{P(OEt)_3\}_4]BPh_4$	3207 m	ν_{NH}	10.93 s, br	=NH	A_2BC	δ_A 83.8
				4.06 m	CH_2		δ_B 76.7
				3.90 m			δ_C 75.6
				1.31 t	CH_3		$J_{AB} = 42.5$
				1.27 t			$J_{AC} = 42.2$
				1.25 t			$J_{BC} = 45.6$

(*continued on next page*)

Table 1 (*continued*)

	Compound	IR[a] (cm^{-1})	Assgnt	^{1}H NMR[b,c] δ (J, Hz)	Assgnt	Spin system	^{31}P{^{1}H} NMR[b,d] δ (J, Hz)
9a	$[IrHCl(\eta^1\text{-}NH{=}CPh_2)\{P(OEt)_3\}(PPh_3)_2]BPh_4$	3243 m	ν_{NH}	8.55 s, br	=NH	AB_2	δ_A 52.9
		2236 w	ν_{IrH}	3.16 qnt	CH_2		δ_B −1.1
				0.67 t	CH_3		J_{AB}=30.1
				AB_2X spin syst	IrH		
				(X = ^{1}H)			
				δ_X −18.75			
				$J_{AX} = 10$			
				$J_{BX} = 20$			
9b	$[IrHCl(\eta^1\text{-}NH{=}CPh_2)\{PPh(OEt)_2\}(PPh_3)_2]BPh_4$	3238 m	ν_{NH}	9.04 s, br	=NH	AB_2	δ_A 80.7
		2243 w	ν_{IrH}	3.41 m	CH_2		δ_B −2.6
				3.09 m			$J_{AB} = 23.0$
				0.72 t	CH_3		
				AB_2X spin syst	IrH		
				(X = ^{1}H)			
				δ_X −19.25			
				$J_{AX} = 10$			
				$J_{BX} = 22$			
10a	$[IrHCl(\eta^1\text{-}NH{=}CPh_2)\{P(OEt)_3\}(AsPh_3)_2]BPh_4$	3250 m	ν_{NH}	9.52 d	=NH	A	18.7 s
				$J_{PH} = 2$			
				3.54 qnt	CH_2		
				0.96 t	CH_3		
				−19.56 d	IrH		
				$J_{PH} = 22$			
10b	$[IrHCl(\eta^1\text{-}NH{=}CPh_2)\{PPh(OEt)_2\}(AsPh_3)_2]BPh_4$	3217 m	ν_{NH}	9.10 s	=NH	A	82.6 s
		2243 w	ν_{IrH}	3.56 m	CH_2		
				0.68 t	CH_3		
				−19.82 d	IrH		
				$J_{PH} = 24$			
11	$[IrH_2(\eta^1\text{-}NH{=}CPh_2)(PPh_3)_3]BPh_4$	3258 m	ν_{NH}	10.61 s	=NH	A_2B	δ_A 2.6
		2170 w	ν_{IrH}	A_2BXY spin syst	IrH_2		δ_B −0.2
				(X, Y = ^{1}H)			$J_{AB} = 12.6$
				δ_X −12.21			
				δ_Y −19.88			
				$J_{XY} = 5.1$			
				$J_{XA} = 20.1$			
				$J_{XB} = 134.1$			
				$J_{YA} = 20.4$			
				$J_{YB} = 10.9$			
12	$[Re\{(CH_3)_2C(H)NH_2\}(CO)_2\{PPh(OEt)_2\}_3]BPh_4$	3298 m	ν_{NH}	4.00 m	CH_2	A_2	140.5 s
		3246 m		2.71 m	CH		
		1956 s	ν_{CO}	2.37 br	NH_2		
		1877 s		1.31 t	CH_3 phos		
				0.90 d	$(CH_3)_2CH$		
13	$[RuH(Ph_2C(H)NH_2)\{P(OEt)_3\}_4]BPh_4$	3323 m	ν_{NH}	4.88 m	CH	AB_2C	δ_A 148.7
		3267 m		4.10–3.60 m	CH_2		δ_B 142.2
		1870 m	ν_{RuH}	1.21 t	CH_3		δ_C 135.6
				1.17 t			$J_{AB} = 64.9$
				1.13 t			$J_{AC} = 34.8$
				−7.40 to −8.44 m	RuH		$J_{BC} = 48.0$
14	$[RuH\{(CH_3)_2C(H)NH_2\}\{P(OEt)_3\}_4]BPh_4$	3342 m	ν_{NH}	4.15–3.80 m	CH_2	AB_2C	δ_A 149.1
		3283 m		2.64 m	CH		δ_B 142.9
		1887 m	ν_{RuH}	2.47 s, br	NH_2		δ_C 137.0
				1.35–1.12 m	CH_3 phos		$J_{AB} = 64.1$
				1.12 d	$(CH_3)_2CH$		$J_{AC} = 36.5$
				−7.51 to −8.55 m	RuH		$J_{BC} = 46.9$

[a] In KBr pellets.

[b] In CD_2Cl_2 at 25 °C.

[c] Phenyl proton resonances of phosphite ligands between 7.70 and 7.20 ppm are omitted.

[d] Positive shifts downfield from 85% H_3PO_4.

[e] At −70 °C.

[f] ^{13}C{^{1}H} NMR, δ: 223.4, 215.8 (m, CO), 187.4 (br, C=N), 160–121 (m, Ph), 66.3, 65.7 (d, CH_2), 16.5, 16.2 (s, br, CH_3).

[g] ^{13}C{^{1}H} NMR, δ: 191.8 (t, $J_{CP} = 8$), 190.1 (t, $J_{CP} = 10$) (CO), 183.2 (t, $J_{CP} = 2$, C=N), 155–122 (m, Ph), 62.8 (m, CH_2), 16.1 (m, CH_3).

[h] ^{13}C{^{1}H} NMR, δ: 196.4 (m), 192.9 (dt) (CO), 184.8 (dt, C=N), 136–122 (m, Ph), 65.7 (d), 63.5 (dt) (CH_2), 16.7, 16.3 (d, CH_3).

a medium-intensity band at 3285–3219 cm^{-1} attributed to the ν_{NH} of the imine ligand, and a weak band at 1987–1911 cm^{-1} due to the ν_{MH} of the hydride group. The ^1H NMR spectra confirm the presence of both imine and hydride ligands, showing the slightly broad signal of the NH proton resonance of the coordinate $Ph_2C{=}NH$ species at 10.87–10.40 ppm and a multiplet of the H^- ligand between −7.11 and −9.07 ppm. In the temperature range between +20 and −80 °C, the ^{31}P NMR spectra of complexes **5** and **6** appear as AB_2C or A_2BC multiplets, indicating the mutually *cis* position of the hydride and imine ligands. On the basis of these data, a geometry of type **III** (Scheme 2) may be proposed for hydride-imine complexes **5** and **6**.

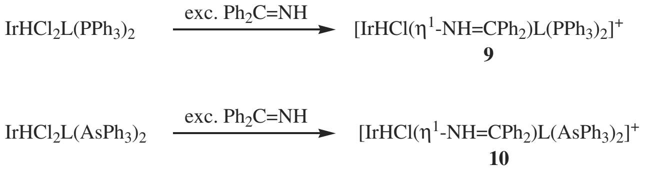
A *cis* arrangement of the imine and triflate ligands, as in type **V**, geometry can also be proposed for the $[Os(\kappa^1\text{-}OTf)(\eta^1\text{-}NH{=}CPh_2)P_4]BPh_4$ complex **8**, whose ^{31}P NMR spectrum appears as an A_2BC multiplet simulable with the parameters reported in Table 1.

The IR spectrum of the bis(imine) $[Ru(\eta^1\text{-}NH{=}CPh_2)_2P_4](BPh_4)_2$ (**7**) derivative shows the ν_{NH} band of the imine at 3223 cm^{-1}, whereas the ^1H NMR spectrum exhibits the NH proton resonance as a slightly broad signal at 10.46 ppm. Surprisingly, the ^{31}P NMR spectra give an asymmetric ABC_2 pattern, which does not change in profile when sample temperature is lowered from +20 to −80 °C. This ABC_2-type ^{31}P spectrum is unexpected, because either a symmetric A_2B_2 or an A_4-type spectrum is expected for octahedral bis(imine) complex **7**. However, the difference in chemical shift between nuclei A and B of our ABC_2 spectrum is very small (Table 1) and the two J_{AC} and J_{BC} values are very similar, suggesting that a *cis* geometry (**IV**) is probably present in our bis(imine) complex **7**, but the steric requirements of the two benzophenone imines cause some distortion on the molecule. Thus, only two phosphines are magnetically equivalent, giving an ABC_2 spectrum for the complex.

Imine complexes of ruthenium and osmium are rare and, apart from Taube's pentamine $[Os(NH_3)_5\{NH{=}C(H)CH_3\}]^{2+}$ complex [2a], only a few examples are known [2f,2g]. The use of phosphite-containing MHP_4 and MP_4 (M = Ru and Os) metal fragments allows easy synthesis of both mono and bis(benzophenone imine) complexes **5**–**8**. It is worth noting that the same MHP_4 and MP_4 fragments were shown to be able to stabilize aryldiazene ligands, giving $[MH(NH{=}NAr)P_4]^+$ and $[M(NH{=}NAr)_2\text{-}P_4]^{2+}$ derivatives [4b,4c,4f], highlighting the fact that a metal fragment that coordinates diazene is also able to bind imine species, giving stable derivatives.

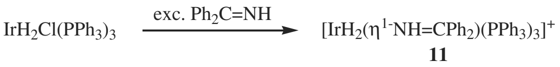
3.2. Iridium complexes

Hydride $IrHCl_2L(PPh_3)_2$ and $IrHCl_2L(AsPh_3)_2$ complexes react with a slight excess of $Ph_2C{=}NH$ to give mono-imine $[IrHCl(\eta^1\text{-}NH{=}CPh_2)L(PPh_3)_2]^+$ (**9**) and $[IrHCl(\eta^1\text{-}NH{=}CPh_2)L(AsPh_3)_2]^+$ (**10**) cations, which were separated as BPh_4 salts and characterized (Scheme 5).



L = $P(OEt)_3$ (**a**), $PPh(OEt)_2$ (**b**).

Scheme 5.

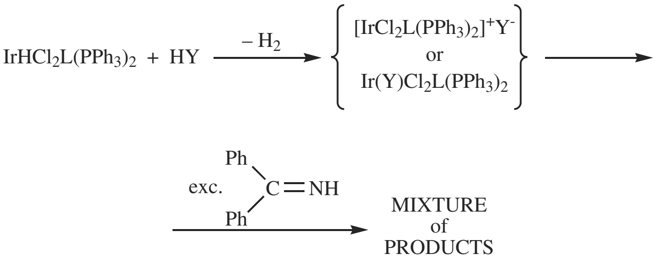


Scheme 6.

The benzophenone imine $Ph_2C{=}NH$ substitutes only one chloride in the starting complex, giving cationic compounds **9**, **10** in good yields. Substitution of the Cl^- ligand also takes place in the dihydride $IrH_2Cl(PPh_3)_3$ species (Scheme 6), giving the imine $[IrH_2(\eta^1\text{-}NH{=}CPh_2)\text{-}(PPh_3)_3]^+$ (**11**) derivatives.

Results in synthesizing imine complexes **1**–**8** using triflate species as starting materials prompted us to use this method also for iridium $IrHCl_2L(PPh_3)_2$ precursors. Treatment of $IrHCl_2L(PPh_3)_2$ complexes with Brønsted acids HY ($Y = BF_4^-$, OTf^-) proceeded with the evolution of H_2 and formation of unsaturated $[IrCl_2L(PPh_3)_2]^+$ cations or neutral $Ir(Y)Cl_2L(PPh_3)_2$ intermediates [5a]. However, reaction of these intermediates with $Ph_2C{=}NH$ gave a mixture of compounds which were not separate in pure form (Scheme 7). The NMR spectra of the reaction products indicated not only other compounds, but also at least two species containing coordinate imine.

This method was therefore abandoned, owing to the formation of too many species. Substitution of the chloride ligand in $IrHCl_2L(PPh_3)_2$ or $IrH_2Cl(PPh_3)_3$ complexes seemed to be the most suitable method for synthesizing mono-imine derivatives of iridium. This method is also important because it allowed the synthesis of the first examples, to the best of our knowledge, of N-proton imine complexes of iridium [1,2].



L = $P(OEt)_3$, $PPh(OEt)_2$; HY = $HBF_4{\bullet}Et_2O$ or HOTf

Scheme 7.

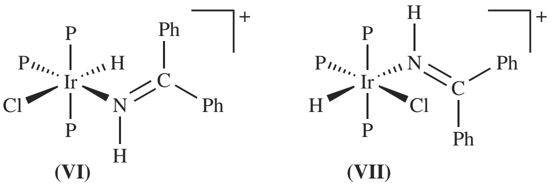

(VI) **(VII)**

Chart 2.

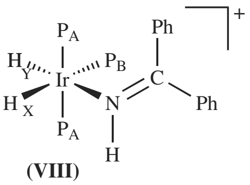

(VIII)

Chart 3.

Imine complexes **9**–**11** are yellow solids, stable in air and in solution of polar organic solvents, where they behave as 1:1 electrolytes [13]. Analytical and spectroscopic data (Table 1) support the proposed formulation.

The IR spectra of the imine complexes of iridium $IrHCl(\eta^1\text{-}NH{=}CPh_2)L(PPh_3)_2$ (**9**) show a medium-intensity band between 3243 and 3238 cm^{-1}, attributed to the ν_{NH} of the imine group, and a weak absorption at 2243–2236 cm^{-1}, due to the ν_{IrH} of the hydride ligand. The presence of both these ligands was confirmed by proton NMR spectra, which show a slightly broad singlet at 9.04–8.55 ppm, due to imine proton resonance. In addition to the signals of the phosphine and the BPh_4 anion, a multiplet also appears in the spectra at −18.75 (**9a**) and −19.25 (**9b**) ppm, attributed to the hydride ligand. As the $^{31}P\{^1H\}$ NMR spectra are AB_2 multiplets, the hydride pattern in the proton spectra may be simulated with an AB_2X model ($X = {}^1H$) using the parameters of Table 1. The values of the two J_{PH} observed in the spectra are comparable, suggesting that the hydride is in a mutually *cis* position with respect to all the phosphorus nuclei of the phosphine. However, these data do not allow us unambiguously to assign one of the two geometries, **VI** or **VII**, to complexes **9** (Chart 2).

The ν_{NH} band at 3250–3217 cm^{-1} was also observed in the arsine $IrHCl(\eta^1\text{-}NH{=}CPh_2)L(AsPh_3)_2$ (**10**) complexes, whose ^1H NMR spectra show the broad NH proton signal of the imine at 9.52–9.10 ppm. Instead, the hydride signal appears as a doublet near −19 ppm, due to coupling with the only phosphite ligand present on the complex, in agreement with the proposed formulation.

The IR spectrum of the dihydride $[IrH_2(\eta^1\text{-}NH{=}CPh_2)(PPh_3)_3]BPh_4$ (**11**) complex shows a medium-intensity band at 3258 cm^{-1}, attributed to the ν_{NH} of the imine group, and a weak absorption at 2170 cm^{-1}, due to the ν_{IrH} of the hydride ligand. The ^1H NMR spectrum shows a slightly broad signal at 10.61 ppm, attributed to NH imine proton resonance, and a complicated multiplet between −11 and −21 ppm, attributed to the two hydride ligands. As the $^{31}P\{^1H\}$ NMR spectrum appears as an A_2B pattern, the hydride multiplet may be simulated with an A_2BXY model (X=H;Y=H) using the parameters of Table 1. The two hydride ligands are magnetically non-equivalent and, on the basis of the ^{31}P spectra, a geometry of type **VIII** (Chart 3) may be proposed for our imine-dihydride complex **11**.

Reactivity studies of imine complexes **9**–**11** toward hydrogenation reactions were made, in order to verify whether amine can form in mild conditions. However, at room temperature no reaction was observed with H_2 at 1 atm and the imine complexes were recovered unchanged after 24 h of reaction. Complexes **1**–**11** were also unreactive toward both substitution of ligands and deprotonation of the imine hydrogen atom by NEt_3 or LiOH, highlighting the considerable stability of the coordinate imine group.

4. Conclusions

This paper describes the synthesis of a series of mono and bis(benzophenone imine) complexes of manganese, rhenium, ruthenium and osmium by substituting a labile triflate ligand on appropriate precursors. The first examples of benzophenone imine complexes of iridium were also prepared, and a geometry in solution was established.

Acknowledgements

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