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Synthesis and reactivity of new benzophenone imine derivatives containing the $Ru(CO)(P^iPr_3)_2$ unit

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Abstract

The five-coordinate bis(alkynyl) complex $Ru(C_2Ph)_2(CO)CP^iPr_3)_2$ (**1**) reacts with benzophenone imine to give $Ru(C_2Ph)\{NH=C(Ph)C_6H_4\}(CO)(P^iPr_3)_2$ (**2**), which affords $Ru(FBF_3)\{NH=C(Ph)C_6H_4\}(CO)(P^iPr_3)_2$ (**3**) and phenylacetylene by reaction with $HBF_4 \cdot OEt_2$. The addition of Lewis bases such as CO, MeCN and $P(OMe)_3$ to dichloromethane solutions of **3** leads to $[Ru\{NH=C(Ph)C_6H_4\}(CO)L(P^iPr_3)_2]BF_4$ (L = CO (**4**), MeCN (**5**)) and $[Ru\{NH=C(Ph)C_6H_4\}(CO)\{P(OMe)_3\}_2(P^iPr_3)]BF_4$ (**6**). Complex **3** also reacts with MeLi to give $Ru(Me)\{NH=C(Ph)C_6H_4\}(CO)(P^iPr_3)_2$ (**7**), which affords $RuH\{NH=C(Ph)C_6H_4\}(CO)(P^iPr_3)_2$ (**8**) by treatment with methanol. In this complex, the hydrido ligand is disposed *trans* to the orthometallated phenyl ring. The reaction of the five-coordinate hydrido–chloro complex $RuHCl(CO)(P^iPr_3)_2$ (**9**) with $LiN=CPh_2$ leads to the azavinylidene derivative $RuH(=N=CPh_2)(CO)(P^iPr_3)_2$ (**10**). Complex **10** is unstable in methanol and evolves to a mixture of **8** and its isomer $RuH\{NH=C(Ph)C_6H_4\}(CO)(P^iPr_3)_2$ (**11**), containing the hydrido ligand *cis* disposed to the orthometallated phenyl ring. This isomer can be obtained as an analytically pure solid in the presence of triisopropylphosphine. The reaction of **9** with benzophenone imine leads to $RuHCl(CO)(NH=CPh_2)(P^iPr_3)_2$ (**12**), which reacts with $AgBF_4$ to give $[RuH(CO)(NH=CPh_2)(P^iPr_3)_2]BF_4$ (**13**). The reaction of **13** with carbon monoxide affords $[RuH(CO)_2(NH=CPh_2)(P^iPr_3)_2]BF_4$ (**14**).

Keywords: Benzophenone imine; Orthometallation; Ruthenium–hydride complexes

1. Introduction

Reactions of late transition metal complexes with terminal alkynes have attracted a great deal of attention in recent years [1–15]. Much of this stems from their potential applications in the material science field [16] and from the fact that they have been found to be key intermediates in the oligomerization [2–12], cyclotrimerization [17], hydrosilylation [18], and hydrostannation [19] of alkynes. Recently, it has also been suggested that these types of compound can play a major role in the reduction of terminal alkynes by hydrogen transfer and hydrogenation with molecular hydrogen [20].

We have previously reported that the treatment of $RuCl_3 \cdot H_2O$ with triisopropylphosphine in refluxing methanol leads to the five-coordinate hydrido–chloro complex $RuHCl(CO)(P^iPr_3)_2$ in good yield [21]. This complex, which is an active and highly selective catalyst for the reduction of unsaturated organic substrates [22] and for the addition of $HSiEt_3$ to phenylacetylene [23], has also been the master key for the development of an extensive organometallic chemistry, including alkynyl [17,24], alkenyl [25], acetatoalkenyl [26], carbene, vinylcarbene [27], acetatocarbene [26], acyl [28], π-butadiene [29], dihydrogen [30], and mono- and binuclear tetrahydridoborato [31,32] complexes. Thus, for example, the reaction of the five-coordinate hydrido–chloro complex $RuHCl(CO)(P^iPr_3)_2$ with sodium tetrahydridoborato leads to the octahedral complex $RuH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2$ [31], which affords the bis(alkynyl) derivative $Ru(C_2Ph)_2(CO)(P^iPr_3)_2$ by reaction with phenylacetylene. At room temperature, $Ru(C_2Ph)_2(CO)(P^iPr_3)_2$ undergoes addition of Lewis bases that are not too bulky (e.g. CO, $P(OMe)_3$, PMe_3) to form compounds of formula $Ru(C_2Ph)_2(CO)L(P^iPr_3)_2$ and $Ru(C_2Ph)_2(CO)(PMe_3)_2(P^iPr_3)$ [24]. In the presence of acetic acid, $Ru(C_2Ph)_2(CO)(P^iPr_3)_2$ gives the acetato-alkynyl derivative $Ru(\eta^2\text{-}$

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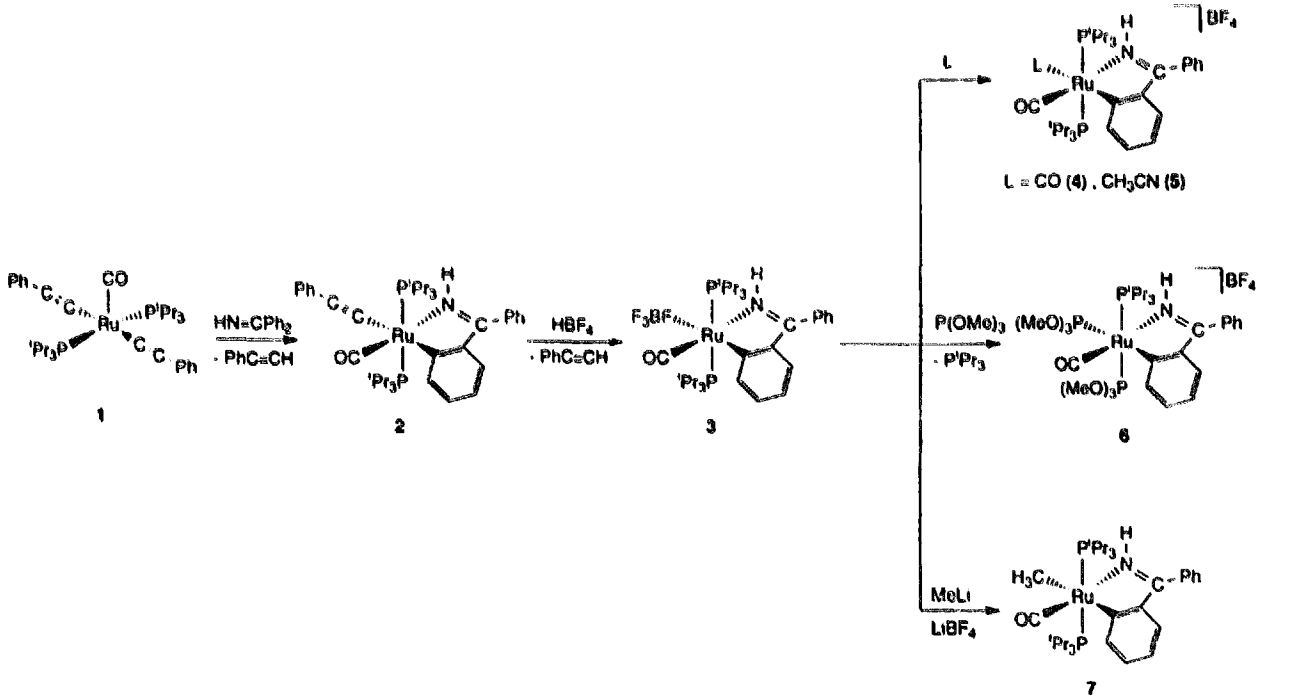
$O_2CMe)(C_2Ph)(CO)(P^iPr_3)_2$, which by protonation with HBF_4 in acetone leads to the acetatoalkenyl $[Ru\{C(=CHPh)OC(O)Me\}(CO)(\eta^1\text{-}OCMe_2)(P^iPr_3)_2]BF_4$. The acetone molecule of this complex can be displaced by the chloride anion to give $Ru\{C(=CHPh)OC(O)Me\}Cl(CO)(P^iPr_3)_2$. The protonation of this complex with HBF_4 in dichloromethane affords the carbene compound $[RuCl(=CH_2Ph)OC(O)Me)(CO)(P^iPr_3)_2]BF_4$ [26].

As a continuation of our work on the five-coordinate bis(alkynyl) complex $Ru(C_2Ph)_2(CO)(P^iPr_3)_2$, and with the intention of expanding the chemistry of the five-coordinate hydrido–chloro complex $RuHCl(CO)(P^iPr_3)_2$ towards benzophenone imine derivatives, we report in this paper on the synthesis and reactivity of the complexes $Ru(C_2Ph)\{NH=C(Ph)C_6H_4\}(CO)(P^iPr_3)_2$, $RuH(=N=CPh_2)(CO)(P^iPr_3)_2$ and $RuHCl(CO)(NH=CPh_2)(P^iPr_3)_2$.

2. Results and discussion

2.1. Synthesis and reactivity of $Ru(C_2Ph)\{NH=C(Ph)C_6H_4\}(CO)(P^iPr_3)_2$

Treatment of a boiling toluene solution of the five-coordinate bis(alkynyl) complex $Ru(C_2Ph)_2(CO)(P^iPr_3)_2$ (**1**) with 1 equiv. of benzophenone imine for 3 h leads to a red solution, from which the orthometallated complex $Ru(C_2Ph)\{NH=C(Ph)C_6H_4\}(CO)(P^iPr_3)_2$ (**2**, Scheme 1) was isolated as an orange solid in 80% yield. The most noticeable absorptions in the IR spectrum of **2**, in Nujol, are three bands at 3328, 2080 and 1915 cm^{-1}, which are assigned to the ν(N–H), ν(C≡C) and ν(CO) vibrations respectively. The ^1H NMR spectrum in benzene-d_6 shows a broad singlet at 9.11 ppm, which is assigned to the NH proton, along with the resonances due to the phenyl groups and the triisopropylphosphine ligands. In the region δ 215–180, the $^{13}C\{^1H\}$ NMR spectrum contains three triplets at 211.80 (J_{P-C} = 14.5 Hz), 196.58 (J_{P-C} = 8.3 Hz) and 184.12 (J_{P-C} = 3.0 Hz). According to the value of the P–C coupling constant, the triplet at 184.2 ppm is assigned to the carbon atom of the C=N group. The chemical shift of this resonance is in agreement with those previously reported for the complexes $[Ru\{N(Ph)=C(R)C_6H_3\}(\eta^6\text{-}C_6Me_6)(PMe_3)]BF_4$ (R = H (175.3 ppm), CH_3 (180.4 ppm)) [33], $[Os\{N(Ph)=C(Ph)C_6H_4\}(\eta^6\text{-}C_6H_3Me_3)(P^iPr_3)]BF_4$ (191.72 ppm, J_{P-C} = 1.5 Hz) [34], $Ru(\eta^5\text{-}C_5H_5)\{NH=C(Ph)C_6H_4\}(PPh_3)$ (183.24 ppm, J_{P-C} = 2.0 Hz) [35] and $OsH\{NH=C(Ph)C_6H_4\}(CO)(P^iPr_3)_2$ (181.15 ppm) [36]. The triplet at lowest field (211.80 ppm) is assigned to the carbonyl group, while the triplet at 196.58 ppm is assigned to the carbon atom of the phenyl ligand directly linked to the metallic center. The spectrum also contains the resonances due to the alkynyl ligand, which appear at 127.52 ppm (C_α) and 116.41 ppm (C_β) as triplets with P–C coupling constants of 18.7 Hz and 1.6 Hz respectively. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 42.3 ppm,



Scheme 1.

indicating that the two phosphine ligands are equivalent and are mutually *trans* disposed. The spectroscopic data of **2** are in agreement with those previously reported for the analogous osmium derivative $Os(C_2Ph)\{NH{=}C(Ph)C_6H_4\}(CO)(P^iPr_3)_2$, where the mutually *trans* disposition of the alkynyl group of the orthometallated phenyl group has been proved by X-ray diffraction [37].

Orthometallated benzophenone imine complexes are rare. They have generally been prepared from azavinylidene derivatives, by treatment with carboxilic acids or methanol [34–36,38,39]. The presence of the electrophilic reagent in these transformations suggests that the reactions involve the initial electrophilic attack of a proton at the nitrogen atom of the azavinylidene group, to give an imine intermediate which evolves by C–H activation into the orthometallated benzophenone imine complex. The replacement of an alkynyl group in **1** by an orthometallated benzophenone imine ligand most probably involves a hydrido-bis(alkynyl) intermediate of ruthenium(IV), which could be generated by coordination of the nitrogen donor ligand, followed by C–H activation of one of the two phenyl groups of the imine. This intermediate should thus afford **2** by reductive elimination of phenylacetylene. A similar mechanism has been proposed for the formation of $Os(C_2Ph)\{NH{=}C(Ph)C_6H_4\}(CO)(P^iPr_3)_2$ [37].

Complex **2** reacts with the stoichiometric amount of a HBF_4 diethyl ether solution to give phenylacetylene and the derivative $Ru(FBF_3)\{NH{=}C(Ph)C_6H_4\}(CO)(P^iPr_3)_2$ (**3**, Scheme 1). Coordination of $[RC{\equiv}C]^-$ to a metallic center transfers the nucleophilicity from the C_α carbon atom to the C_β carbon atom. Thus, the addition of electrophiles to alkynyl complexes has been described on many occasions and is considered the most convenient method for the synthesis of vinylidene complexes [40]. The formation of phenylacetylene from the reaction of **2** with HBF_4 implies acceptance of the fact that when the alkynyl group is coordinated to the fragment $Ru\{NH{=}C(Ph)C_6H_4\}(CO)(P^iPr_3)_2$, the transfer of nucleophilicity from C_α to C_β is not efficient or, alternatively, that the H^+ attack takes place at the ruthenium atom of **2**. In the latter case, the formation of **4** should involve a ruthenium(IV) hydrido-alkynyl intermediate.

The elimination of phenylacetylene, compared with the orthometallated phenyl ring, from this ruthenium(IV) hydrido-alkynyl intermediate merits further consideration. The increased s character of the sp hybrid causes this orbital to be less directional than the sp^2 hybrid and, therefore, the sp hybrid can have more multicentered bonding at the transition state, leading to lower activation energies for the elimination. This could explain why the elimination of phenylacetylene is more favored than the elimination of the orthometallated phenyl ring of the imine in **2**. The same type of argument has been used to rationalize the elimination of styrene from the reaction of $Ru(Me)\{(E)\text{-}CH{=}CHPh\}(CO)_2(P^iPr_3)_2$ with HBF_4 [28] and the following observations [41]: (i) the reductive elimination of toluene from *cis*-$Ni(CH_3)(C_6H_5)L_2$ is faster than the elimination of ethane from *cis*-$Ni(CH_3)_2L_2$ [42]; (ii) the reaction of PhLi with $PdCl_2$(DIPHOS) yields biphenyl directly, whereas MeLi reacts with $PdCl_2$(DIPHOS) to afford $PdMe_2$(DIPHOS) which eliminates ethane slowly [43]; and (iii) platinum diphenylbis(phosphine) complexes can eliminate biphenyl [44], while platinum dimethylbis(phosphine) complexes are very stable [45].

A similar behavior to that described for **2** has previously been observed for the related osmium complex $Os(C_2Ph)\{NH{=}C(Ph)C_6H_4\}(CO)(P^iPr_3)_2$ [37], for some alkynyl ruthenium(II) complexes [26], for d^5 high-spin anionic acetylide complexes of manganese(II), and for metals of Groups 11 and 12, where the reactions with acids lead to the quantitative liberation of alkynes RC≡CH [1].

The reaction of **2** with HBF_4 was carried out in diethyl ether as solvent, and complex **3** was isolated as a yellow solid in 48% yield. The presence of a coordinated $[FBF_3]^-$ anion in **3** was inferred from the IR spectrum in Nujol of the compound, which contains three very strong bands at 1110, 1095 and 1020 cm^{-1}, a characteristic pattern for a coordinated $[FBF_3]^-$ anion with C_{3v} symmetry [46]. The IR spectrum also shows absorptions at 3320 and 1930 cm^{-1}, corresponding to the ν(N–H) and ν(CO) vibrations respectively. The ^1H NMR spectrum in chloroform-*d* contains the resonances due to the triisopropylphosphine ligands and the phenyl groups, along with a broad signal at 10.81 ppm, assigned to the NH proton. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 36.2 ppm.

The FBF_3 ligand of **3** is easily displaced by Lewis bases (Scheme 1). By passing a slow stream of carbon monoxide through a dichloromethane solution of **3**, the dicarbonyl complex $[Ru\{NH{=}C(Ph)C_6H_4\}(CO)_2(P^iPr_3)_2]BF_4$ (**4**) is formed. The *cis* relative position of the carbonyl ligands was inferred from the IR spectrum, which shows, along with a ν(N–H) band at 3280 cm^{-1}, two strong ν(CO) absorptions at 2030 and 1965 cm^{-1}, a typical pattern for mononuclear *cis* dicarbonyl complexes. Furthermore, the spectrum contains the absorption due to the $[BF_4]^-$ anion. In contrast to that of **3**, this anion gives rise to only one band centered at 1050 cm^{-1}, supporting the fact that, in this case, the anion is not coordinated to the metallic center. In agreement with the IR spectrum, the $^{13}C\{^1H\}$ NMR spectrum of **4** shows two triplets at 203.22 ($J_{P\text{-}C}$ = 11.5 Hz) and 196.12 ($J_{P\text{-}C}$ = 10.6 Hz), attributable to the carbonyl ligands. This spectrum also contains the expected resonances for the orthometallated benzophenone imine ligand. The C=N carbon atom appears at 188.35 ppm as a triplet with a P–C coupling constant

of 2.6 Hz, and the carbon atom of the phenyl ring directly linked to the ruthenium atom appears at 178.39 ppm as a triplet with a P–C coupling constant of 10.1 Hz. The CH groups of the phosphine ligands give a virtual triplet at 25.50 ppm ($N = 21.6$ Hz), which is characteristic of two equivalent phosphine ligands in a relative *trans* position. This is in agreement with the singlet at 39.6 ppm found in the $^{31}P\{^1H\}$ NMR spectrum. In the ^1H NMR spectrum, the most noticeable resonance is due to the NH proton, which lies at 9.11 ppm.

The addition of acetonitrile to **3** leads to $[Ru\{NH{=}C(Ph)C_6H_4\}(MeCN)(CO)(P^iPr_3)_2]BF_4$ (**5**). This complex was isolated as a yellow solid in 70% yield. In the IR spectrum, in Nujol, the most noticeable absorptions are three bands at 3280, 2360 and 1920 cm^{-1}, which are assigned to the ν(N–H), ν(C≡N) and ν(C≡O) vibrations respectively, together with the absorption due to the $[BF_4]^-$ anion with T_d symmetry between 1100 and 1000 cm^{-1}. The ^1H NMR spectrum shows the expected resonances due to the phosphine ligands and the phenyl groups, along with a broad singlet at 10.31 ppm (NH) and a singlet at 2.54 ppm (CH_3CN). In the $^{13}C\{^1H\}$ NMR spectrum the carbon atom of the C≡N group and the carbon atom of the phenyl group linked to the ruthenium atom appear at 184.05 and 182.65 ppm as triplets with P–C coupling constants of 3.0 and 9.0 Hz respectively. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 35.3 ppm.

The reaction of **3** with trimethylphosphite produces not only the substitution of the FBF_3 ligand from the coordination sphere of the ruthenium but also the displacement of one of the two phosphine ligands. Thus, the treatment of **3** with 2 equiv. of trimethylphosphite in dichloromethane at room temperature leads to $[Ru\{NH{=}C(Ph)C_6H_4\}(CO)(P(OMe)_3)_2(P^iPr_3)]BF_4$ (**6**), which was isolated as a yellow solid in 62% yield. The IR spectrum of **6** in Nujol shows absorptions at 3340 and 1975 cm^{-1} corresponding to the ν(N–H) and ν(CO) vibrations respectively, along with the absorption due to the $[BF_4]^-$ anion with T_d symmetry centered at 1050 cm^{-1}. In agreement with the presence of two chemically inequivalent trimethylphosphite groups in **6**, the ^1H NMR spectrum of this compound shows two doublets ($J_{P-H} = 10.4$ Hz) at 3.81 and 3.61 ppm, and the $^{31}P\{^1H\}$ NMR spectrum shows three double doublets. Two of them, due to the trimethylphosphite groups, appear at 136.2 ppm ($J_{P-P} = 47.2$ and 34.3 Hz) and 123.4 ppm ($J_{P-P} = 353.0$ and 47.2 Hz), and the third one corresponding to the triisopropylphosphine ligand is located at 35.9 ppm. The relative *trans* position of one of the two trimethylphosphite ligands and the orthometallated phenyl ring is strongly supported by the $^{13}C\{^1H\}$ NMR spectrum, which shows a doublet of double doublets at 180.03 ppm with P–C coupling constants of 99.2, 16.1 and 15.2 Hz.

Complex **3** also reacts with methyllithium. The treatment of a toluene solution of **3** with 1 equiv. of methyllithium at room temperature affords the methyl derivative $Ru(Me)\{NH{=}C(Ph)C_6H_4\}(CO)(P^iPr_3)_2$ (**7**, Scheme 1), which was isolated by addition of hexane as an orange solid in 62% yield. The most noticeable absorptions in the IR spectrum of **7** in Nujol are the ν(N–H) and ν(CO) vibrations, which appear at 3320 and 1885 cm^{-1} respectively. In the ^1H NMR spectrum in benzene-d_6, the NH proton is observed as a broad resonance at 8.70 ppm, and the protons of the methyl ligand give rise to a triplet at 0.11 ppm, with a P–H coupling constant of 5.7 Hz. The $^{13}C\{^1H\}$ NMR spectrum shows the resonance due to the carbon atom of the methyl group at −15.90 ppm as a triplet with a P–C coupling constant of 12.0 Hz. This spectrum also contains the resonances due to the carbon atoms of the C=N group and the phenyl group linked to the metallic center, which appear at 182.65 and 202.64 ppm as triplets with P–C coupling constants of 3.2 and 8.3 Hz respectively. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 40.0 ppm.

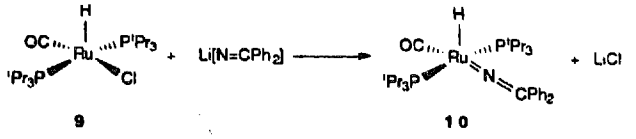
Complex **7** is related to the osmium derivative $Os(Me)\{NH{=}C(Ph)C_6H_4\}(CO)(P^iPr_3)_2$ [37]. However, there is a marked difference in reactivity between them towards methanol. Whereas the osmium complex is stable in methanol, the ruthenium analogue evolves into the hydrido derivative $RuH\{NH{=}C(Ph)C_6H_4\}(CO)(P^iPr_3)_2$ (**8**) (Eq. (1)). A similar reaction had previously been used to prepare the dihydrido–iron(II) compound $FeH_2(PMe_3)_4$ and its osmium analogue starting from the hydrido-alkyl derivatives $[MH(\eta^2\text{-}CH_2PMe_2)(PMe_3)_3]$ (M = Fe [47], Os [48]).

7 8 (1)

Complex **8** was isolated as an orange solid in 60% yield. The IR spectrum in Nujol contains bands at 3323, 2018 and 1889 cm^{-1}, which are assigned to the ν(N–H), ν(Ru–H) and ν(CO) vibrations respectively. In the ^1H NMR spectrum, the most noticeable resonances are a broad singlet at 8.40 ppm, corresponding to the NH proton, and a triplet at −5.94 ppm with a P–H coupling constant of 23.7 Hz due to the hydrido ligand. In the $^{13}C\{^1H\}$ NMR spectrum, the carbon atom of the C=N group and the carbon atom directly linked to the ruthenium atom appear at 183.20 and 208.84 ppm, as triplets with P–C coupling constants of 1.8 and 6.0 Hz respectively. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 64.3 ppm, which under off-resonance conditions is split into a doublet due to the P–H coupling.

2.2. Synthesis and reactivity of $RuH(=N=CPh_2)(CO)(P^iPr_3)_2$

Treatment of a tetrahydrofuran solution of $Li[N=CPh_2]$ with the five-coordinate complex $RuHCl(CO)(P^iPr_3)_2$ (**9**) in a 1:1 molar ratio for 30 min gives a sticky residue after solvent removal. Hexane extraction of the residue and filtration to remove the salt LiCl affords a brown solution, from which the azavinylidene complex $RuH(=N=CPh_2)(CO)(P^iPr_3)_2$ (**10**) was isolated at −78 °C as brown crystals in 52% yield (Eq. (2)). The complexes $OsH(=N=CPh_2)(CO)(P^iPr_3)_2$ [36], $Zr(\eta^5\text{-}C_5H_5)_2(=N=CPh_2)_2$ [49] and $[Os(=N=CPh_2)(\eta^6\text{-}C_6H_6)(P^iPr_3)]X$ (X = PF_6 [34], I [38]) have been similarly prepared starting from $OsHCl(CO)(P^iPr_3)_2$, $Zr(\eta^5\text{-}C_5H_5)_2Cl_2$ and $OsI_2(\eta^6\text{-}C_6H_6)(P^iPr_3)$ respectively.

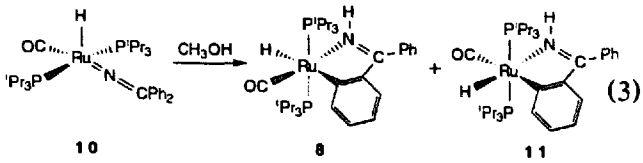


(2)

We assume that the coordination geometry around the ruthenium atom is square-pyramidal with the hydrido ligand in the apical position and the azavinylidene group disposed *trans* to the carbonyl ligand. This is in agreement with previous results obtained by Caulton and coworkers [50] on related systems $RuHX(CO)(P^tBu_2Me)_2$, where the high stability of the *trans* X–CO disposition seems to be the result of a push–pull mechanism between the π-donor X ligand and the π-acceptor CO group. In addition, we have observed that for this kind of system, in the sixth (formally unoccupied) position of the octahedron, the metallic center is well shielded. Four of the 12 methyl groups of the triisopropylphosphine ligands surround the metal like an umbrella [25,27,28].

The azavinylidene group has a great π-donor power. Thus, it is generally viewed as a three-electron donor ligand [51]. Although complex **10** is five-coordinate, this π-donor power of the azavinylidene group makes the molecule not truly a 16-valence electron species. In agreement with this, the ^1H NMR spectrum of **10** shows the hydrido resonance at −14.40 ppm (t, J_{P-H} = 18.1 Hz), shifted by 9.8 ppm towards low field compared with that of the starting complex **9** (−24.20 ppm [21]), which is generally considered as a 16-valence electron compound. The $^{13}C\{^1H\}$ NMR spectrum shows the resonance due to the carbon atom of the C=N group at 160.12 ppm as a triplet with a P–C coupling constant of 5.3 Hz. The CH groups of the phosphine ligands give a virtual triplet at 26.15 ppm (N = 19.6 Hz), which is characteristic of two equivalent phosphine ligands in a *trans* relative position. In accordance with this, the $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 62.5 ppm, which under off-resonance conditions, due to the P–H coupling, is split into a doublet.

Complex **10** is unstable in methanol and evolves to a mixture of the hydrido orthometallated benzophenone imine derivatives **8** and **11** (Eq. (3)).



(3)

Characteristic features of **11** are three absorptions in the IR spectrum at 3315, 1982 and 1889 cm^{-1}, which are assigned to the vibrations ν(N–H), ν(Ru–H) and ν(CO) respectively. The ^1H NMR spectrum shows a broad singlet at 9.88 ppm due to the NH group, and a triplet at −11.05 ppm with a P–H coupling constant of 24.6 Hz, corresponding to the hydrido ligand. The resonance of the hydrido ligand of **11** is shifted by 5.11 ppm towards high field compared with that of the hydrido ligand of **8**. This is in agreement with the fact that an aryl group has a higher *trans*-effect than a nitrogen-donor ligand. In the $^{13}C\{^1H\}$ NMR spectrum, the carbon atom of the C=N group and the carbon atom directly linked to the ruthenium atom appear at 180.83 and 198.33 ppm as triplets with P–C coupling constants of 1.8 and 13.9 Hz respectively. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 56.0 ppm, which under off-resonance conditions is split into a doublet, due to the P–H coupling.

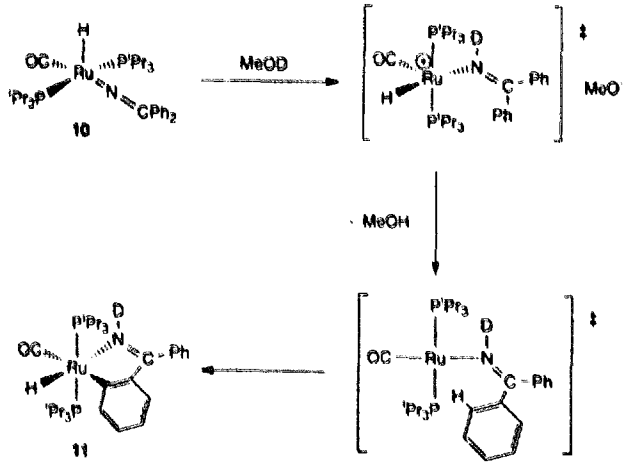
We have previously mentioned that the formation of hydrido orthometallated benzophenone imine derivatives from azavinylidene complexes in the presence of alcohols involves the initial electrophilic attack of the alcohol to the nitrogen atom of the azavinylidene group. According to this, we have also observed that, in methanol-d_4 as solvent, complex **10** gives **8**-d_1 and **11**-d_1, both compounds containing the deuterium atom at the nitrogen atom. This fact is proved by the IR spectrum of the mixture, which shows two ν(N–D) bands at 2439 and 2465 cm^{-1}. The abstraction of the hydrido ligand with the base MeO^- could afford the ruthenium(0) intermediate $Ru(CO)(ND=CPh_2)(P^iPr_3)_2$. The subsequent C–H activation of the *ortho*-CH bond of the phenyl group of the imine should give **11**, which contains the hydrido ligand and the orthometallated ring mutually *cis* disposed (Scheme 2).

C–H activation reactions are generally concerted processes, which lead to products containing the hydrido and η^1-carbon ligands mutually *cis* disposed. Therefore, the formation of **8**, which contains the hy-

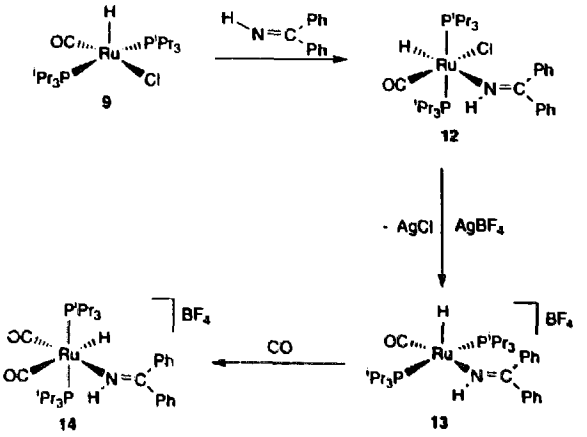
drido ligand and the orthometallated ring mutually *trans* disposed, cannot be rationalized by a similar pathway to that mentioned above for **11**. At first glance, one may think that **8** is a result of the isomerization of **11** in methanol. However, this must be ruled out because **11** is stable in methanol and isomerization into **8** is not observed. Hence, it could be proposed that the formation of **8** takes place in a similar way to the orthopalladation reactions. That is, an electrophilic substitution catalyzed by bases, which proceeds by unsaturated intermediates of 14-valence electrons [52]. The base acts as a hydrogen acceptor and in our case could be MeO^-, generated from the protonation of the nitrogen atom of the azavinylidene group. This nitrogen atom should also be the leading group for the metallation. The presence of free coordinating molecules during the reaction inhibits the orthopalladation process [52]. In agreement with this, we have also observed that the reaction of the azavinylidene complex **10** with methanol in the presence of triisopropylphosphine exclusively affords **11**.

2.3. Synthesis and reactivity of $RuHCl(CO)(NH{=}CPh_2)(P^iPr_3)_2$

Although monodentate nitrogen-bound imine complexes are rare as a result of the weak Lewis basicity of the imine nitrogen atom [53], the addition of benzophenone imine to a hexane suspension of **9** leads to the yellow complex $RuHCl(CO)(NH{=}CPh_2)(P^iPr_3)_2$ (**12**, Scheme 3) in 81% yield. The IR spectrum of **12** shows absorptions at 3230, 2052 and 1900 cm^{-1}, which are assigned to the ν(N–H), ν(Ru–H) and ν(CO) respectively. The ^1H NMR spectrum in toluene-d_8 is temperature dependent. At room temperature the NH proton and the hydrido ligand give rise to broad resonances at 11.50 and −13.21 ppm respectively. At −80 °C the high field resonance is converted into a triplet with a P–H coupling constant of 22.2 Hz, this suggests that in solution **12** is stable only at low temperature. At room



Scheme 2.



Scheme 3.

temperature, there is a dynamic equilibrium which involves **12** and **9**. The $^{31}P\{^1H\}$ NMR spectrum of **12** shows a singlet at 52.6 ppm, indicating that the two phosphine ligands are equivalent.

Complex **12** reacts with 1 equiv. of $AgBF_4$ in acetone to give the five-coordinate cationic complex $[RuH(CO)(NH{=}CPh_2)(P^iPr_3)_2]BF_4$ (**13**), which was isolated as a yellow solid in 58% yield. The non-coordination of the $[BF_4]^-$ anion to the ruthenium atom is strongly supported by the IR spectrum of **13**, which contains the characteristic bands of this anion with T_d symmetry between 1100 and 1000 cm^{-1}. In the ^1H NMR spectrum, the most noticeable resonances are a broad signal at 10.39 ppm, corresponding to the NH proton, and a triplet at −16.09 ppm with a P–H coupling constant of 18.9 Hz due to the hydrido ligand. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 51.3 ppm.

The coordination number six for the ruthenium can be achieved by reaction with carbon monoxide. By passing a slow stream of this gas through a dichloromethane solution of **13**, the *cis*-dicarbonyl complex $[RuH(CO)_2(NH{=}CPh_2)(P^iPr_3)_2]BF_4$ (**14**) is formed. The *cis* relative position of the carbonyl ligands was inferred from the IR spectrum, which shows, along with the ν(N–H) and ν(Ru–H) bands at 2325 and 2040 cm^{-1}, two strong ν(CO) absorptions at 1980 and 1935 cm^{-1}. Furthermore, the spectrum contains the absorption due to the $[BF_4]^-$ anion with T_d symmetry between 1100 and 1000 cm^{-1}. In the ^1H NMR spectrum, the NH resonance appears at 9.44 ppm, whereas the hydrido ligand gives rise to a triplet at −5.33 ppm with a P–H coupling constant of 18.9 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 58.2 ppm.

3. Conclusion

This study shows that the five-coordinate complexes $Ru(C_2Ph)_2(CO)(P^iPr_3)_2$ and $RuHCl(CO)(P^iPr_3)_2$ react

with benzophenone imine to afford new benzophenone imine derivatives containing the $Ru(CO)(P^iPr_3)_2$ unit. Thus, we report new neutral orthometallated benzophenone imine complexes stabilized by alkynyl, methyl, hydrido and tetrafluoroborato ligands and related cationic derivatives. In addition, the preparation of the azavinylidene compound $RuH(=N=CPh_2)(CO)(P^iPr_3)_2$ and new neutral and cationic imine compounds is also described.

4. Experimental details

All reactions were carried out with rigorous exclusion of air by using Schlenk tube techniques. Solvents were dried by known procedures and distilled under argon prior to use. The starting materials $Ru(C_2Ph)_2(CO)(P^iPr_3)_2$ (1) [24] and $RuHCl(CO)(P^iPr_3)_2$ (9) [21] were prepared by published methods. Benzophenone imine (Aldrich) was used without further purification.

NMR spectra were recorded on a Varian UNITY 300 spectrometer. Chemical shifts are expressed in parts per million upfield from Me_4Si ($^{13}C\{^1H\}$, ^1H) and 85% H_3PO_4 ($^{31}P\{^1H\}$). Coupling constants J and N are given in hertz. Infrared spectra were run on a Perkin–Elmer 783 spectrophotometer (Nujol mulls on polyethylene sheets). C, H and N analyses were carried out with a Perkin–Elmer 240C microanalyzer.

4.1. Preparation of $Ru(C_2Ph)\{NH=C(Ph)C_6H_4\}(CO)(P^iPr_3)_2$ (2)

A solution of $Ru(C_2Ph)_2(CO)(P^iPr_3)_2$ (1) (97 mg, 0.15 mmol) in 8 ml of toluene was treated with the stoichiometric amount of $NH=CPh_2$ (26 μl, 0.15 mmol). After 3 h of reaction at the reflux temperature (110 °C), the red solution that formed was evaporated to dryness. Addition of MeOH caused the precipitation of an orange product. The solid was washed with MeOH and dried in vacuo. Yield 87.7 mg (80%). Anal. Found: C, 66.04; H, 8.43; N, 1.80. $C_{40}H_{57}NOP_2Ru$ Calc.: C, 65.73; H, 7.86; N, 1.91%. IR (Nujol, cm^{-1}): ν(NH) 3328(w); ν(C≡C) 2080(m); ν(CO) 1915(s). ^1H NMR (300 MHz, C_6D_6, 20 °C): δ 9.11 (br s, 1H, N*H*), 7.6–6.9 (m, 14H, Ph), 2.31 (m, 6H, PC*H*$(CH_3)_2$), 1.55 (dvt, 18H, N = 14.0 Hz, J_{HH} = 7.1 Hz, PCH(C*H*$_3)_2$), 0.81 (dvt, 18H, N = 12.1 Hz, J_{HH} = 6.6 Hz, PCH(C*H*$_3)_2$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ 42.3 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2): δ 211.80 (t, J_{CP} = 14.5 Hz, CO), 196.58 (t, J_{CP} = 8.3 Hz, Ru–C_{ortho}), 184.12 (t, J_{CP} = 3.0 Hz, C=NH), 145.81, 144.51, 139.02, 131.55, 131.09, 130.93, 130.20, 128.27, 127.99 (all s, aromatic C), 127.52 (t, J_{PC} = 18.7 Hz, RuC≡), 123.76, 120.16 (both s, aromatic C), 116.41 (t, J_{PC} = 1.6 Hz, ≡CPh), 25.14 (vt, N = 20.2 Hz, PCH$(CH_3)_2$), 20.85, 18.98 (both s, PCH(C*H*$_3)_2$).

4.2. Preparation of $Ru(FBF_3)\{NH=C(Ph)C_6H_4\}(CO)(P^iPr_3)_2$ (3)

A solution of $Ru(C_2Ph)\{NH=C(Ph)C_6H_4\}(CO)(P^iPr_3)_2$ (2) (200 mg, 0.27 mmol) in 20 ml of diethyl ether was treated with the stoichiometric amount of a diethyl ether solution of HBF_4 (37 μl, 0.27 mmol). After stirring for 4 h a yellow solid precipitated. This product was washed with diethyl ether and dried in vacuo. Yield 93 mg (48%). Anal. Found: C, 53.80; H, 7.45; N, 1.83. $C_{32}H_{52}BF_4NOP_2Ru$ Calc.: C, 53.64; H, 7.31; N, 1.95%. IR (Nujol, cm^{-1}): ν(NH) 3320(w); ν(CO) 1930(s); $\nu(BF_4)$ 1110(s) 1095(s) 1020(s). ^1H NMR (300 MHz, $CDCl_3$, 20 °C): δ 10.81 (s, 1H, N*H*), 7.8–6.8 (m, 9H, Ph), 2.43 (m, 6H, PC*H*$(CH_3)_2$), 1.13 (dvt, 18H, N = 14.1 Hz, J_{HH} = 7.1 Hz, PCH(C*H*$_3)_2$), 0.98 (dvt, 18H, N = 13.4 Hz, J_{HH} = 7.0 Hz, PCH(C*H*$_3)_2$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): 36.2 (s).

4.3. Preparation of $[Ru\{NH=C(Ph)C_6H_4\}(CO)_2(P^iPr_3)_2]BF_4$ (4)

A slow stream of carbon monoxide was bubbled through a solution of $Ru(FBF_3)\{NH=C(Ph)C_6H_4\}(CO)(P^iPr_3)_2$ (3) (143 mg, 0.20 mmol) in 8 ml of CH_2Cl_2 for 10 min. The solution was evaporated to ca. 0.5 ml. The addition of diethyl ether caused the precipitation of a pale yellow solid that was washed with diethyl ether and dried in vacuo. Yield 106 mg (71%). Anal. Found: C, 53.11; H, 7.34; N, 1.78. $C_{33}H_{52}BF_4NO_2P_2Ru$ Calc.: C, 53.23; H, 7.04; N, 1.88%. IR (Nujol, cm^{-1}): ν(NH) 3280(w); ν(CO) 2030(vs) 1965(vs); $\nu(BF_4)$ 1100–1000(vs). IR (CH_2Cl_2, cm^{-1}): ν(CO) 2020(vs) 1980(vs). ^1H NMR (300 MHz, $CDCl_3$, 20 °C): δ 9.90 (s, 1H, N*H*), 8.19–7.10 (m, 9H, Ph), 2.18 (m, 6H, PC*H*$(CH_3)_2$), 1.22 (dvt, 18H, N = 14.3 Hz, J_{HH} = 7.2 Hz, PCH(C*H*$_3)_2$), 1.03 (dvt, 18H, N = 12.5 Hz, J_{HH} = 6.9 Hz, PCH(C*H*$_3)_2$). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 39.6 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 203.22 (t, J_{CP} = 11.5 Hz, CO), 196.18 (t, J_{CP} = 10.6 Hz, CO) 188.35 (t, J_{CP} = 2.6 Hz, C=NH), 178.39 (t, J_{CP} = 10.1 Hz, Ru–C_{ortho}), 145.02, 142.43, 134.94, 132.81, 131.58, 130.95, 129.42, 127.96, 124.09, 121.23 (all s, aromatic C), 25.50 (vt, N = 21.6 Hz, PCH$(CH_3)_2$), 19.64, 18.93 (both s, PCH(C*H*$_3)_2$).

4.4. Preparation of $[Ru\{NH=C(Ph)C_6H_4\}(MeCN)(CO)(P^iPr_3)_2]BF_4$ (5)

A solution of $Ru(FBF_3)\{NH=C(Ph)C_6H_4\}(CO)(P^iPr_3)_2$ (3) (80 mg, 0.11 mmol) in 5 ml of MeCN was stirred for 10 min. Then, the solvent was evaporated to dryness. The addition of diethyl ether caused the precipitation of a yellow solid that was washed with diethyl ether and dried in vacuo. Yield 58.3 mg (70%). Anal. Found: C, 54.03; H, 7.17; N, 3.65. $C_{34}H_{55}BF_4N_2OP_2Ru$

Calc.: C, 53.90; H, 7.32; N, 3.70%. IR (Nujol, cm^{-1}): ν(NH) 3280(w); ν(C≡N) 2360(w); ν(CO) 1920(s); $\nu(BF_4)$ 1100–1000(vs). ^1H NMR (300 MHz, $CDCl_3$, 20°C): δ 10.31 (s, 1H, N*H*), 8.1–6.9 (m, 9H, Ph), 2.54 (s, 3H, CH_3CN), 2.18 (m, 6H, PC*H*$(CH_3)_2$), 1.29 (dvt, 18H, N = 13.9 Hz, J_{HH} = 7.1 Hz, PCH(C*H*$_3)_2$), 1.04 (dvt, 18H, N = 12.6 Hz, J_{HH} = 6.8 Hz, PCH(C*H*$_3)_2$). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 35.3 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 206.69 (t, J_{CP} = 13.8 Hz, CO), 184.05 (t, J_{CP} = 3.0 Hz, C=NH), 182.65 (t, J_{CP} = 9.0 Hz, Ru–C_{ortho}), 144.24, 142.58, 136.05, 131.95, 131.09, 130.91, 129.18 (all s, aromatic C), 128.61 (s, CH_3CN), 128.09, 121.23 (both s, aromatic C), 24.30 (vt, N = 19.8 Hz, P*C*H$(CH_3)_2$), 19.78, 18.71 (both s, PCH(*C*H$_3)_2$), 3.69 (s, *C*H$_3$CN).

4.5. Preparation of [Ru{NH=C(Ph)C$_6$H$_4$}(CO){P(OMe)$_3$}$_2$(P^{i}Pr$_3$)]BF$_4$ (6)

A solution of Ru(FBF$_3$){NH=C(Ph)C$_6$H$_4$}(CO)(P^{i}Pr$_3$)$_2$ (**3**) (95 mg, 0.13 mmol) in 6 ml of CH_2Cl_2 was treated with a 2:1 excess of P(OMe)$_3$ (29 μl, 0.24 mmol). After 8 h of reaction, the resulting yellow solution was evaporated to ca. 0.5 ml. The addition of diethyl ether caused the precipitation of a pale yellow solid that was washed with diethyl ether and dried in vacuo. Yield 65 mg (62%). Anal. Found: C, 43.76; H, 6.35; N, 1.72. $C_{29}H_{45}BF_4NO_7P_3Ru$ Calc.: C, 43.30; H, 6.14; N, 1.74%. IR (Nujol, cm^{-1}): ν(NH) 3340(w); ν(CO) 1975(s); $\nu(BF_4)$ 1100–1000(vs). ^1H NMR (300 MHz, $CDCl_3$, 20°C): δ 8.71 (s, 1H, N*H*), 8.10–7.02 (m, 9H, Ph), 3.81 (d, 9H, J_{PH} = 10.4 Hz, P(OC*H*$_3)_3$), 3.61 (d, 9H, J_{PH} = 10.4 Hz, P(OC*H*$_3)_3$), 2.18 (m, 3H, PC*H*$(CH_3)_2$), 1.06 (m, 18H, PCH(C*H*$_3)_2$). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 136.29 dd, $J_{P_1P_2}$ = 47.2 Hz, $J_{P_3P_1}$ = 34.3 Hz, P(3)), 123.4 (dd, $J_{P_2P_1}$ = 353.0 Hz, $J_{P_2P_3}$ = 47.2 Hz, P(2)), 35.9 (dd, $J_{P_1P_2}$ = 353.0 Hz, $J_{P_1P_3}$ = 34.3 Hz, P(1)). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 203.81 (m, CO), 188.72 (m, C=NH), 180.03 (ddd, J_{CP_1} = 99.2 Hz, J_{CP_2} = 16.1 Hz, J_{CP_3} = 15.2 Hz, Ru=C_{ortho}), 145.19, 142.17, 136.37 (all s, aromatic C), 131.89 (d, J_{PC} = 4.7 Hz, C_{ipso}-Ph), 131.24 (s, aromatic C), 130.58 (d, $J_{P,C}$ = 6.7 Hz, C_{meta}-Ph), 129.45, 127.33, 123.19 (all s, aromatic C), 54.01 (d, J_{PC} = 9.2 Hz, P(OCH$_3)_3$), 53.14 (d, J_{PC} = 8.0 Hz, P(OCH$_3)_3$), 25.34 (d, J_{PC} = 17.0 Hz, PCH$(CH_3)_2$), 19.12, 17.78 (both s, PCH(*C*H$_3)_2$).

4.6. Preparation of Ru(Me){NH=C(Ph)C$_6$H$_4$}(CO)(P^{i}Pr$_3$)$_2$ (7)

A solution of Ru(FBF$_3$){NH=C(Ph)C$_6$H$_4$}(CO)(P^{i}Pr$_3$)$_2$ (**3**) (85 mg, 0.12 mmol) in 10 ml of toluene was treated with the stoichiometric amount of MeLi (74 μl, 0.12 mmol). After 10 min of reaction, the resulting suspension was filtered through Kieselguhr and evaporated to dryness. The addition of hexane caused the precipitation of an orange solid which was dried in vacuo. Yield 48 mg (62%). Anal. Found: C, 62.08; H, 8.20; N, 2.07. $C_{33}H_{55}NOP_2Ru$ Calc.: C, 61.47; H, 8.60; N, 2.17%. IR (Nujol, cm^{-1}): ν(NH) 3320(w); ν(CO) 1885(s). ^1H NMR (300 MHz, C_6D_6, 20°C): δ 8.70 (s, 1H, N*H*), 8.91–7.14 (m, 9H, Ph), 2.13 (m, 6H, PC*H*$(CH_3)_2$), 1.26 (dvt, 18H, N = 13.4 Hz, J_{HH} = 7.6 Hz, PCH(C*H*$_3)_2$), 0.87 (dvt, 18H, N = 12.3 Hz, J_{HH} = 6.8 Hz, PCH(C*H*$_3)_2$), 0.11 (t, 3H, J_{PH} = 5.7 Hz, C*H*$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 40.0 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 214.96 (t, J_{CP} = 16.1 Hz, CO), 202.64 (t, J_{CP} = 8.3 Hz, Ru–C_{ortho}), 182.65 (t, J_{CP} = 3.2 Hz, C=NH), 145.99, 144.45, 139.63, 131.24, 129.64, 129.03, 128.51, 127.80, 119.71 (all s, aromatic C), 24.75 (vt, N = 18.0 Hz, P*C*H$(CH_3)_2$), 20.52, 19.08 (both s, PCH(*C*H$_3)_2$), −15.90 (t, J_{PC} = 12.0 Hz, *C*H$_3$).

4.7. Preparation of RuH{NH=C(Ph)C$_6$H$_4$}(CO)(P^{i}Pr$_3$)$_2$ (8)

A suspension of Ru(Me){NH=C(Ph)C$_6$H$_4$}(CO)(P^{i}Pr$_3$)$_2$ (**7**) (70 mg, 0.11 mmol) in 6 ml of MeOH was left to stir for 20 min at room temperature. An orange solid separated. This product was washed with MeOH and dried in vacuo. Yield 42 mg (60%). Anal. Found: C, 60.54; H, 9.28; N, 2.16. $C_{32}H_{53}NOP_2Ru$ Calc.: C, 60.94; H, 8.47; N, 2.22%. IR (Nujol, cm^{-1}): ν(NH) 3323(w); ν(RuH) 2018(w); ν(CO) 1889(s). ^1H NMR (300 MHz, C_6D_6, 20°C): δ 8.40 (s, 1H, N*H*), 8.3–6.8 (m, 9H, C_6H_5), 2.02 (m, 6H, PC*H*$(CH_3)_2$), 1.32 (dvt, 18H, N = 12.9 Hz, J_{HH} = 6.3 Hz, PCH(C*H*$_3)_2$), 0.97 (dvt, 18H, N = 12.3 Hz, J_{HH} = 5.3 Hz, PCH(C*H*$_3)_2$), −5.94 (t, 1H, J_{PH} = 23.7 Hz, Ru*H*). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ 64.3 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6): δ 211.07 (t, J_{CP} = 14.3 Hz, CO), 208.84 (t, J_{CP} = 6.0 Hz, Ru–C_{ortho}), 183.20 (t, J_{CP} = 1.8 Hz, C=NH), 145.80, 144.83, 140.21, 131.18, 129.03, 128.68, 127.08, 119.12 (all s, aromatic C, one signal corresponding to an aromatic C atom is masked by the resonance of the solvent, C_6D_6), 26.77 (vt, N = 19.8 Hz, P*C*H$(CH_3)_2$), 19.78, 18.90 (both s, PCH(*C*H$_3)_2$).

4.8. Reaction of 8 with MeOH

A suspension of **8** (40 mg, 0.06 mmol) in 5 ml of MeOH was left to stir for 36 h at room temperature. The resulting orange solid was identified by ^1H and $^{31}P\{^1H\}$ NMR spectroscopies as complex **8**.

4.9. Preparation of RuH(CO)(=N=CPh$_2$)(P^{i}Pr$_3$)$_2$ (10)

A solution of NH=CPh$_2$ (34.5 μl, 0.2 mmol) in 6 ml of THF was treated with a slight excess of ^{n}BuLi

(0.2 ml, 0.32 mmol, 1.6 M in hexane). The initially colorless solution turned red, and then the stoichiometric amount of **9** (100 mg, 0.2 mmol) was added. After stirring for 30 min the solvent was removed and the crude was extracted in 40 ml of hexane. The suspension was filtered through Kieselguhr and evaporated to 1 ml. Light brown crystals were obtained when the solution was cooled to −78 °C for 24 h. The crystals were washed carefully with 1 ml of cold hexane and dried in vacuo. Yield 65.6 mg (52%). Anal. Found: C, 60.57; H, 9.56; N, 2.34. $C_{32}H_{53}NOP_2Ru$ Calc.: C, 60.93; H, 8.47; N, 2.22%. ^{1}H NMR (300 MHz, C_6D_6): δ 7.9–7.0 (m, 10H, C_6H_5), 2.00 (m, 6H, PCH(CH$_3$)$_2$), 1.20 (dvt, 18H, N = 13.7 Hz, J_{HH} = 7.1 Hz, PCH(CH_3)$_2$), 1.00 (dvt, 18H, N = 12.9 Hz, J_{HH} = 6.9 Hz, PCH(CH_3)$_2$), −14.40 (t, 1H, J_{PH} = 18.1 Hz, RuH). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ 62.5 (s). ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6): δ 211.31 (t, J_{PC} = 12.9 Hz, CO), 160.12 (t, J_{PC} = 5.3 Hz, C=N), 139.63, 138.24 (both s, C_{ipso}Ph), 129–127 (m, C_6H_5), 26.15 (vt, N = 19.6 Hz, PCH(CH$_3$)$_2$), 20.86, 19.57 (both s, PCH(CH_3)$_2$).

4.10. Preparation of the isomeric mixture cis- and trans-RuH{NH=C(Ph)C$_6$H$_4$}(CO)(P^{i}Pr$_3$)$_2$ (11, 8)

A solution of **10** (60 mg, 0.09 mmol) in 5 ml of MeOH was left to stir for 3 h at room temperature. The resulting orange solid was washed with MeOH and dried in vacuo. The product was a mixture of **11** and **8**. Yield 44.3 mg (78%). Anal. Found: C, 60.54; H, 9.28; N, 2.16. $C_{32}H_{53}NOP_2Ru$ Calc.: C, 60.94; H, 8.47; N, 2.22%. Spectroscopic data of **11**: IR (Nujol, cm^{-1}): ν(NH) 3315(w); ν(RuH) 1982(w); ν(CO) 1889(s). ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ 9.88 (s, 1H, NH), 8.3–6.8 (m, 9H, C_6H_5), 2.02 (m, 6H, PCH(CH$_3$)$_2$), 1.25 (dvt, 18H, N = 13.0 Hz, J_{HH} = 6.9 Hz, PCH(CH_3)$_2$), 0.97 (dvt, 18H, N = 13.5 Hz, J_{HH} = 7.1 Hz, PCH(CH_3)$_2$), −11.05 (t, 1H, J_{PH} = 24.6 Hz, RuH). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): 56.0 (s). ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6): δ 206.87 (t, J_{CP} = 12.9 Hz, CO), 198.33 (t, J_{CP} = 13.9 Hz, Ru–C_{ortho}), 180.83 (t, J_{CP} = 1.8 Hz, C=NH), 144.57, 143.72, 140.04, 129.33, 128.59, 128.54, 127.07, 126.53, 120.33 (all s, aromatic C), 26.58 (vt, N = 20.3 Hz, PCH(CH$_3$)$_2$), 19.67, 18.69 (both s, PCH(CH_3)$_2$).

4.11. Preparation of the isomeric mixture cis- and trans-RuH{ND=C(Ph)C$_6$H$_4$}(CO)(P^{i}Pr$_3$)$_2$ (11-d_1, 8-d_1)

A solution of **10** (60 mg, 0.09 mmol) in 5 ml of CD$_3$OD was left to stir for 3 h at room temperature. The resulting orange solid was washed with CD$_3$OD and dried in vacuo. Yield 47 mg (80%). Spectroscopic data of **11-d_1**: IR (KBr, cm^{-1}): ν(ND) 2439(w); ν(CO) 1889(s). ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ 8.3–6.8 (m, 9H, C_6H_5), 2.02 (m, 6H, PCH(CH$_3$)$_2$), 1.25 (dvt, 18H, N = 13.0 Hz, J_{HH} = 6.9 Hz, PCH(CH_3)$_2$), 0.97 (dvt, 18H, N = 13.5 Hz, J_{HH} = 7.1 Hz, PCH(CH_3)$_2$), −11.05 (t, 1H, J_{PH} = 24.6 Hz, RuH). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): 56.0 (s). Spectroscopic data of **8-d_1**: IR (KBr, cm^{-1}): ν(ND) 2465(w); ν(CO) 1889(s). ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ 8.3–6.8 (m, 9H, C_6H_5), 2.02 (m, 6H, PCH(CH$_3$)$_2$), 1.32 (dvt, 18H, N = 12.9 Hz, J_{HH} = 6.3 Hz, PCH(CH_3)$_2$), 0.97 (dvt, 18H, N = 12.3 Hz, JHH = 5.3 Hz, PCH(CH_3)$_2$), −5.94 (t, 1H, J_{PH} = 23.7 Hz, RuH). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ 64.3 (s).

4.12. Reaction of 10 with MeOH in the presence of free P^{i}Pr$_3$

A solution of 100 mg (0.16 mmol) of **10** in 5 ml of MeOH was prepared and kept as standard. Simultaneously, another solution of 100 mg (0.16 mmol) of **10** in 5 ml of MeOH was treated with a 1:2 excess of P^{i}Pr$_3$ (57 μl, 0.30 mmol). After stirring for 2 h at room temperature, an orange solid separated from the standard solution. This solid turned out to be a mixture of isomers **11** and **8** in a 2:1 ratio. After stirring for 3 h, an orange solid precipitated from the solution with excess P^{i}Pr$_3$. This solid was identified by ^{1}H and ^{31}P{^{1}H} NMR spectroscopies as isomer **11**.

4.13. Reaction of 11 with MeOH

A suspension of **11** (50 mg, 0.08 mmol) in 5 ml of MeOH was stirred for 12 h at room temperature. The ^{1}H and ^{31}P{^{1}H} NMR spectra of the orange solid that separated from the suspension correspond exactly to isomer **11**.

4.14. Preparation of RuHCl(CO)(NH=CPh$_2$)(P^{i}Pr$_3$)$_2$ (12)

A solution of **9** (204 mg, 0.42 mmol) in 10 ml of hexane was treated with the stoichiometric amount of NH=CPh$_2$ (70.5 μl, 76.1 mg, 0.42 mmol). After stirring for 1 h at room temperature, a yellow solid precipitated. The solid was filtered off, washed with hexane and dried in vacuo. Yield 227 mg (81%). Anal. Found: C, 57.75; H, 8.84; N, 2.09. $C_{32}H_{54}ClNOP_2Ru$ Calc.: C, 57.60; H, 8.16; N, 2.10%. IR (Nujol, cm^{-1}): ν(NH) 3230(w); ν(RuH) 2052(s); ν(CO) 1900(s). ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ 11.50 (s, 1H, NH), 8.0–6.8 (m, 10H, C_6H_5), 2.30 (m, 6H, PCH(CH$_3$)$_2$), 1.20 (dvt, 36H, N = 13.2 Hz, J_{HH} = 6.9 Hz, PCH(CH_3)$_2$), −13.21 (br, 1H, RuH). ^{1}H NMR (300 MHz, C_7D_8, −80 °C): δ 11.50 (s, 1H, NH), 8.0–6.8 (m, 10H, C_6H_5), 2.30 (m, 6H, PCH(CH$_3$)$_2$), 1.20 (dvt, 36H, N = 13.2 Hz, J_{HH} = 6.9 Hz, PCH(CH_3)$_2$), −12.17 (t, 1H, J_{PH} = 22.2 Hz, RuH). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ 52.6 (s).

4.15. Preparation of $[RuH(CO)(NH=CPh_2)(P^iPr_3)_2]BF_4$ (13)

A solution of **12** (200 mg, 0.30 mmol) in 10 ml of acetone was treated with the stoichiometric amount of $AgBF_4$ (60 mg, 0.31 mmol). After stirring for 30 min in the dark at room temperature, the suspension was filtered through Kieselguhr and evaporated to 0.5 ml. The addition of diethyl ether caused the precipitation of a yellow solid that was washed with diethyl ether and dried in vacuo. Yield 125 mg (58%). Anal. Found: C, 53.44; H, 8.45; N, 1.79. $C_{32}H_{54}BF_4NOP_2Ru$ Calc.: C, 53.49; H, 7.57; N, 1.95%. IR (Nujol, cm^{-1}): ν(NH) 3255(w) 3235(w); ν(Ru–H) not observed; ν(CO) 1945(s) 1935(s); $\nu(BF_4)$ 1100–1000(vs). IR (CH_2Cl_2, cm^{-1}): ν(CO) 1965(s). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.39 (s, 1H, N*H*), 7.80–7.40 (m, 10H, C_6H_5) 2.11 (m, 6H, PC*H*(CH_3)$_2$), 1.25 (dvt, 18H, $N = 13.7$ Hz, $J_{HH} = 7.1$ Hz, PCH(C*H*$_3$)$_2$), 1.03 (dvt, 18H, $N = 14.5$ Hz, $J_{HH} = 7.1$ Hz, PCH(C*H*$_3$)$_2$), −16.09 (t, 1H, $J_{PH} = 18.9$ Hz, Ru*H*). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ 51.3 (s).

4.16. Preparation of $[RuH(CO)_2(NH=CPh_2)(P^iPr_3)_2]BF_4$ (14)

A stream of carbon monoxide was bubbled through a solution of **13** (100 mg, 0.14 mmol) in 10 ml of CH_2Cl_2 for 30 min. The solution was then evaporated to 0.5 ml. The addition of diethyl ether caused the precipitation of a pale yellow solid that was washed with diethyl ether and dried in vacuo. Yield 64.4 mg (62%). Anal. Found: C, 52.69; H, 8.07; N, 2.05. $C_{33}H_{54}BF_4NO_2P_2Ru$ Calc.: C, 53.09; H, 7.29; N, 1.88%. IR (Nujol, cm^{-1}): ν(NH) 3325(w); ν(RuH) 2040(m); ν(CO) 1980(s) 1935(s); $\nu(BF_4)$ 1100–1000(vs). IR (CH_2Cl_2, cm^{-1}): ν(CO) 2025(s) 1980(s). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.44 (s, 1H, N*H*), 7.0–7.6 (m, 10H, C_6H_5), 2.16 (m, 6H, PC*H*(CH_3)$_2$), 1.20 (dvt, 36H, $N = 14.1$ Hz, $J_{HH} = 6.9$ Hz, PCH(C*H*$_3$)$_2$), −5.33 (t, 1H, $J_{PH} = 18.9$ Hz, Ru*H*). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ 58.2 (s).

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