Interionic Solution Structure of Acetyl Ru^{II} Complexes Bearing Diimine and Diamine Ligands by ^1H-NOESY and $^{19}F\{^1H\}$-HOESY NMR: Still More Specific Anion−Cation Interactions

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Complexes *trans*-[$Ru(PMe_3)_2(CO)(COMe)(N,N)$]X (N,N = diimine or diamine ligand, $X^- = BF_4^-$ or BPh_4^-) have been synthesized by the reaction of *cis*,*trans*-[$RuI(Me)(CO)_2(PMe_3)_2$] with N,N ligands having different steric and electronic properties. The syntheses were only successful with moderately hindered ligands; in other cases, solvento complexes were formed. Some of these were isolated and characterized. The interionic structures of the aforementioned cationic complexes have been investigated in dichloromethane solution by means of ^1H-NOESY and $^{19}F\{^1H\}$-HOESY NMR experiments. The anion–cation interactions (especially for the diamine complexes) were found to be more specific than those in analogous compounds bearing aromatic N,N ligands. For the first time, we have found that the anion preferentially resides close to the N arm *trans* to the COMe group.

Introduction

Even though the phenomenon of ion-pairing is of great importance in several chemical processes mediated by cationic transition metal complexes,[1] structural studies of such ion pairs in solution are still rare. The principal reason for this is that it is difficult to obtain detailed structural information about ion pairs using classical techniques.

Recently, we showed[2] that direct and detailed structural information about ion pairs containing transition metals can be obtained quite easily using NOE NMR spectroscopy, based on the dependence of the NOE between the interacting nuclei on their distance.[3] In principle, this also makes it possible to investigate the relative structures of non-covalently bonded moieties, such as two charged fragments of an ion pair. In practice, several complications and limitations arise that hamper such investigations to some extent. The first limitation stems from the limit of detection of the NOE, which is ca. 5 Å. Thus, (1) only intimate ion pairs can be investigated. A complication arises if we want to quantify the NOE in order to estimate average interionic distances. Due to the possibility of relative anion−cation motion (2), the rotational correlation times of nuclei belonging to both fragments must be measured in order to check the meaning of the estimated average interionic distances. The first limitation (1) is not so severe because, as might reasonably be assumed, the anion−cation interactions mainly affect the chemical reactivity of the ion-pair under conditions conducive to intimate ion-pair formation (a solvent of moderate dielectric constant, high concentrations, low temperature, etc.). The second complication (2) is more serious,[4] although very often it is not necessary to have explicit knowledge of interionic distances but only of the preferred mutual orientation eventually adopted by the anion and cation. This information can be gleaned in a semi-quantitative manner through observing the NOE contacts (weak, medium, strong, etc.).

Our previous studies were principally carried out on model cationic Ru^{II} compounds bearing bidentate (N,N) or tridentate (N,N,N) ligands,[2a−2e] where the N atoms were incorporated into aromatic rings. These studies were performed in dichloromethane solution, using both symmetrical and unsymmetrical counterions.[2e] In all cases, we observed a remarkable degree of specificity in the NOE interionic contacts. The counterion was found to reside close to the N,N or N,N,N ligands, and, in the case of unsymmetrical counterions, showed a tendency to maximize the lyophilic interactions. With the help of quantum mechanical and molecular mechanics calculations,[2c] we rationalized such specificity in terms of non-centrosymmetric charge distribution and, in particular, an accumulation of positive charge in the aromatic rings containing the N atoms. In order to ascertain whether the presence of N-aromatic ligands is necessary for the delocalization of the positive charge, we decided to synthesize and investigate analogous complexes containing non-aromatic N,N ligands.

In this paper, we report the synthesis and characterization of complexes *trans*-[$Ru(PMe_3)_2(CO)(COMe)(N,N)$]X (N,N = diimine or diamine ligand; see Scheme 1) and the determination of their interionic structure in dichloromethane.

Results and Discussion

Synthesis

The starting material for the synthesis of complexes **2−10** was *cis*,*trans*-[$RuI(Me)(CO)_2(PMe_3)_2$] (**1**).[5] In solvents with

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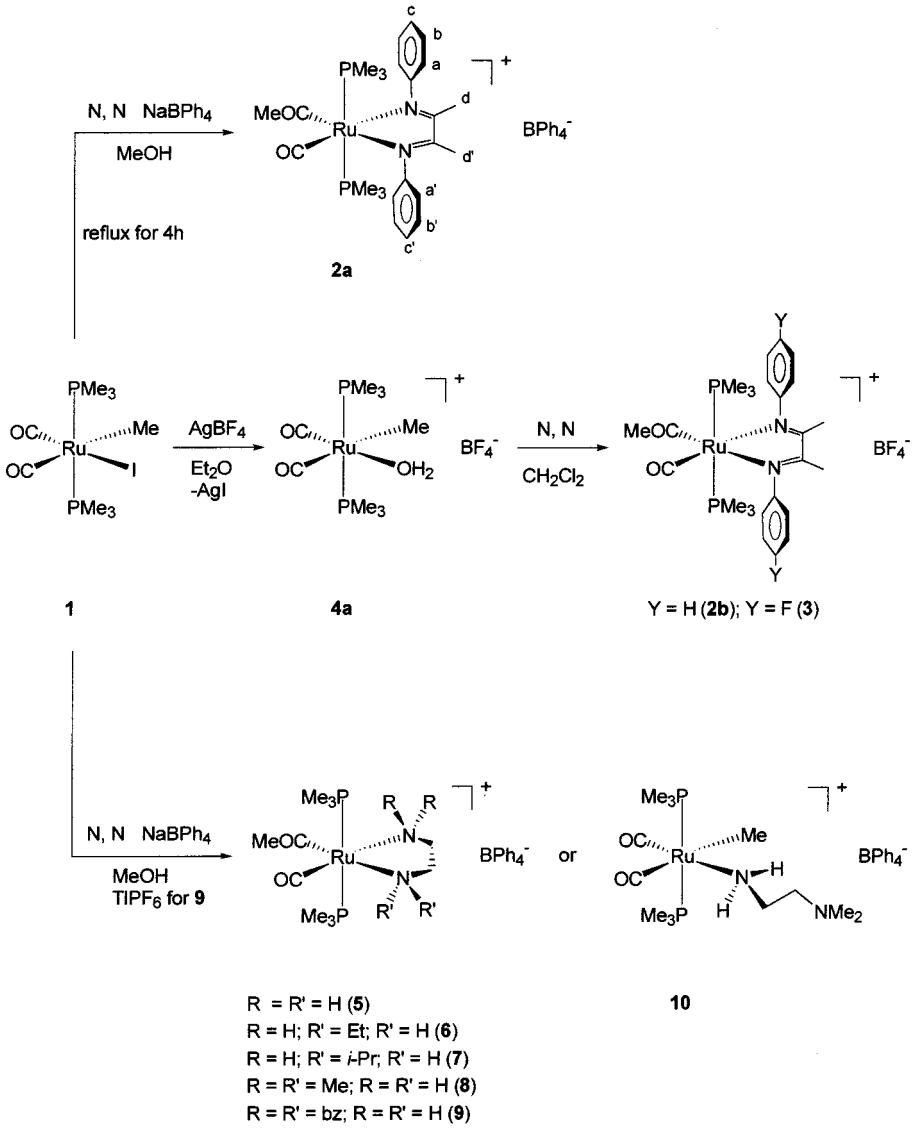


Scheme 1

suitable dielectric constants, complex **1** undergoes dissociation of the Ru−I bond and migration of Me onto a *cis* CO, thereby making two coordination sites available. The reaction of complex **1** with diacetyl bis(phenylimine) ligands in methanol containing excess $NaBPh_4$ at room temperature did not afford the desired acetyl products. Furthermore, it showed that methanol and water may act as competing ligands. The methanolic complex *trans,cis*-[Ru(PMe_3)$_2$(CO)$_2$(Me)(MeOH)]BPh_4 (**4b**) was obtained in good yield by the reaction of complex **1** with $TlPF_6$ in MeOH followed by the addition of a large excess of $NaBPh_4$. By refluxing a methanolic solution of complex **1** for 4 h, complex **2a** was synthesized in low yield (Scheme 1). Complexes **2b**−**3** were synthesized under mild conditions and in acceptable yields by treating **1** with $AgBF_4$ in diethyl ether (see Scheme 1). In each case, the precipitate formed, containing AgI and a solvento complex intermediate, was treated with a solution of the appropriate ligand in dichloromethane. The complexes **2b** or **3** thus obtained were precipitated by adding *n*-hexane. When this synthetic procedure was attempted using diimine ligands bearing substituents in their *ortho* positions (Me, Et, *i*Pr), the reactions were unsuccessful. When the same procedure was carried out in the absence of any ligand, complex **4a** was formed.

The reactions of complex **1** with the diamine ligands were found to proceed quite quickly in methanol at room temperature with *N*-substituted diamines and with *N*,*N*′-disubstituted diamines bearing small substituents (see Scheme 1). In the case of *N*,*N*′-dibenzylethylenediamine, it was found necessary to force the ionization of the Ru−I bond by adding $TlPF_6$ in order to obtain the desired complex in a reasonable time and, consequently, to avoid formation of the methanol complex. The reaction with *N*,*N*-disubstituted ethylenediamine afforded a methyl complex with a η^1-coordinated diamine ligand.

The reactions with both the diimine and diamine ligands indicate that steric factors play a crucial role. In the case of diimine ligands, the interactions of the *ortho* substituents with the acetyl and PMe_3 groups are the limiting factors. In the case of the diamine ligands, the sp^3 nature of the N

atom makes the interaction of the R, R′, and PMe_3 groups the most important. The formation of complex **10** demonstrates that two methyl groups cannot remain on the same coordinated nitrogen.

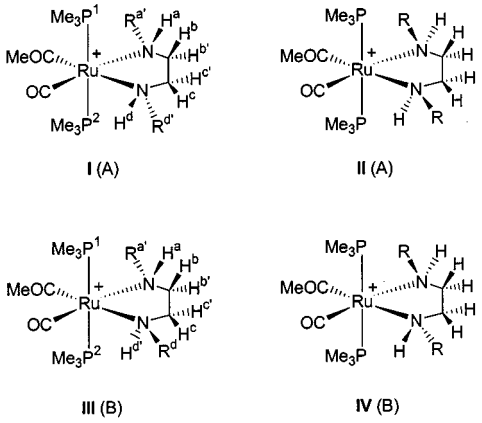
Intramolecular Characterization

The intramolecular characterization was carried out by IR and ^1H, ^{13}C, ^{31}P, and ^{19}F NMR spectroscopy. The structures of complexes **2−9** could easily be established by considering that: (1) two CO stretching bands were observed, one in the typical region for terminal carbonyls and the other in the region for acyl groups; (2) a deceptive triplet,[6] typical of the *trans* position, was observed for PMe_3 in both the ^1H and $^{13}C\{^1H\}$ NMR spectra of complexes **1−5**, while for the other complexes the observed $^2J_{PP}$ coupling constants were consistent with two mutually *trans* PMe_3 groups, and (3) the protons and carbons of the two N arms are chemically non-equivalent. In the ^1H-NOESY spectra of the *N*-substituted complexes **6** and **7**, no contact between the COMe and the substituents was observed. Consequently, the *N*-substituted arm must lie *trans* to the COMe group. An assignment of all the proton and carbon resonances, a prerequisite for a detailed determination of the interionic structure, proved more difficult. This was especially true for complexes with *N*,*N*′-disubstituted ethylenediamine ligands incorporating two chiral nitrogen atoms. In such cases, a pair of racemic diastereoisomers A (I and II) and B (III and IV) are present in solution (see Scheme 2).[7] For example, two species are discernible in the case of complex **8**. The $^{31}P\{^1H\}$ NMR spectrum features two doublets with relative integrals of 1 and another two with relative integrals of 3 (Figure 1). Even though the aliphatic region of the ^1H NMR spectrum is quite complicated, the four doublets of doublets due to the PMe_3 groups and the four doublets due to the Me groups bonded to N atoms are sufficiently resolved. The ^1H-NOESY spectrum (Figure 2) indicates that: (a) one PMe_3 of the more abundant isomer shows NOE contacts with both Me groups while the other shows none; (b) each PMe_3 group of the less abundant isomer shows an NOE contact with one Me group. The major stereoisomers present in solution are those labelled A in Scheme 2, in which the two substituents are oriented towards the same PMe_3 group. In hindsight, it can be seen that for these isomers the difference in chemical shift of the two P nuclei is greater than for the others, due to the higher extent of octahedral distortion of the ligand sphere. By combining the information provided by ^1H-COSY, ^1H-NOESY, and "normal" and long-range ^1H-^{13}C HMQC experiments, and assuming that N−H and N−Me resonances *cis* to COMe resonate at higher frequencies (due to the previously observed deshielding effect of COMe), it was possible to assign most of the resonances (see Exp. Sect.).

Interionic Structure in Solution by NMR

The relative anion−cation orientation (interionic structure) was investigated in dichloromethane solution by detecting interionic "contacts" in the ^1H-NOESY and $^{19}F\{^1H\}$-HOESY NMR spectra. The most significant results can be summarized as follows.

The ^1H-NOESY spectrum of complex **2a** shows (1) that PMe_3 protons interact quite strongly with all the aromatic protons of BPh_4^-, and (2) that the Me groups of the diimine ligand interact with *o*-H and *m*-H (Figure 3). The interactions between the counterion and the aromatic protons



Scheme 2

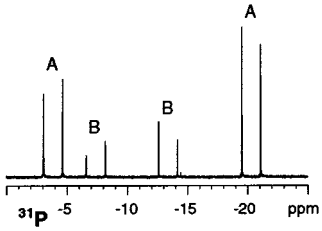


Figure 1. $^{31}P\{^1H\}$ NMR spectrum of complex **8** recorded at 298 K in $[D_2]$dichloromethane showing the presence of two species in a 1:3 ratio

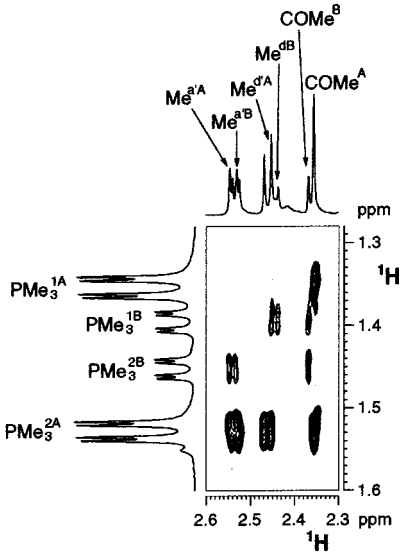


Figure 2. A section of the ^1H-NOESY NMR spectrum of complex **8** recorded at 298 K in $[D_2]$dichloromethane showing the interactions of $PMe_3{}^2$ with both Me groups in the A stereoisomers and the interactions of $PMe_3{}^2$ with $Me^{a'}$ and of $PMe_3{}^1$ with Me^d in the B stereoisomers

of the cation can be detected more readily in the $^{19}F\{^1H\}$-HOESY NMR spectrum of **2b** (Figure 4): BF_4^- shows "contacts" with o^a and $o^{a'}$ and weaker ones with m^b and $m^{b'}$. The same contacts were observed for complex **3**. No contacts were observed between the counterion and the COMe protons or *p*-H or *p*-F in any of the three complexes. The average interionic structure that can be inferred from these observations is one in which the counterion preferentially resides on the side of the N,N ligand above or below the plane defined by the N,N, CO, and COMe ligands.

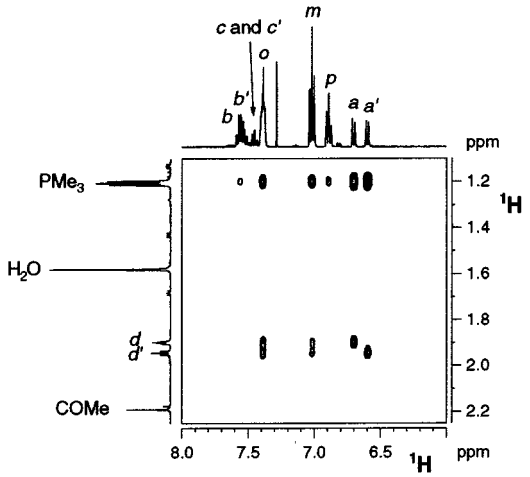


Figure 3. A section of the ^1H-NOESY NMR spectrum of complex **2a** recorded at 298 K in $[D_2]$dichloromethane showing the interionic contacts between the PMe_3 groups and all the aromatic protons of BPh_4^- and between the Me^d protons and *o*-H and *m*-H

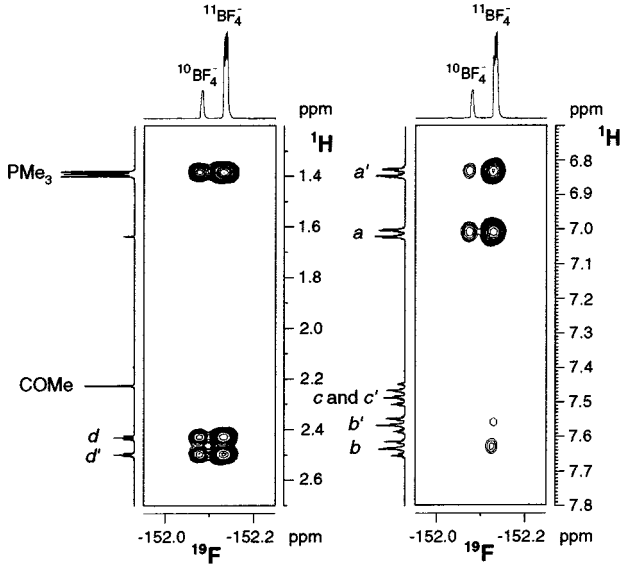


Figure 4. Two sections of the $^{19}F\{^1H\}$-HOESY NMR spectrum of complex **2b** recorded at 298 K in $[D_2]$dichloromethane showing the interionic contacts between BF_4^- and PMe_3 and the *d*, *d'*, *a*, and *a'* protons, as well as weaker contacts with *b* and *b'*

Besides showing strong contacts between PMe_3 and all the aromatic protons of BPh_4^-, the ^1H-NOESY spectrum of complex **5** shows contacts between NH_2^d, CH_2^c, and CH_2^b (very weak) and *o*-H and *m*-H. COMe and NH_2^a do not interact with the counterion (Figure 5). This indicates that the counterion is located close to the N,N ligand and prefers to stay close to the N arm *trans* to the acetyl group.

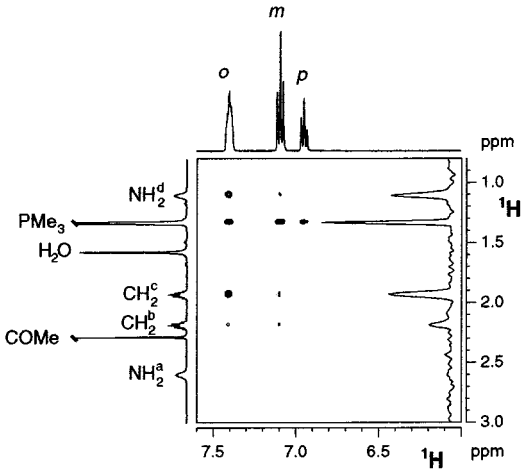


figure 5. A section of the ^1H-NOESY NMR spectrum of complex **5** recorded at 298 K in $[D_2]$dichloromethane showing the gradual decrease of the interionic contact intensity on going from positions *d* to *a*; the 1D trace along the axis corresponding to the *ortho* protons is shown on the right

The ^1H-NOESY spectrum of the two A stereoisomers **8** depicted in Scheme 2 indicates that the counterion shows two preferential interactions, (1) with the protons of the arm *trans* to the COMe group, and (2) with the protons of the less hindered phosphane PMe_3[1]. Once again, there is no interaction with the COMe. The same is true for complex **9**. The position of the counterion is remarkably well defined; it stays on the side of the N,N ligand, shifted towards the arm *trans* to COMe and close to the phosphane that is not hindered by the methyl groups of the N,N ligand.

The interionic structure of the diamine complexes reported here is the most specific that we have never observed in octahedral complexes. The use of non-aromatic N,N ligands does not affect the delocalization of the positive charge that accumulates on the N,N side. In addition, it seems that the positive charge is prevalently delocalized over the N arm *trans* to the COMe group, as indicated by the selective interionic interactions of the protons of this arm with those associated with the counterion.

Conclusions

The use of non-aromatic N,N ligands has unexpectedly led to a higher specificity in the anion−cation interactions, particularly for the diamine complexes. From previous studies,[2c] we know that the stabilization of ion pairs in such complexes is mainly electrostatic, and the fact that the interionic structure is not dependent on the nature of the counterion (BF_4^- or BPh_4^-) further confirms this. The observed specificity can only be attributed to an accumulation of positive charge on the N,N ligands. Not only the lack of unsaturation (as in the diamine ligands) does not affect this accumulation, but it also interrupts the communication be-

tween the two N arms, imparting them with different affinities towards the anion. Steric interactions become important in determining the fine structure, as demonstrated by the interionic structure of the A stereoisomers of complex **9**; here, the electrostatic energy gain directs the counterion to the side of the N,N ligand, while the less hindered P^1-phosphane is favoured by the reduced steric repulsions.

Experimental Section

General Remarks: Complex **1** was prepared according to the literature.[5] Reactions were carried out in dried apparatus under an inert atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were purified by conventional methods prior to use.[8] The diimine ligands were synthesized according to the literature.[9] Diamines were obtained commercially and were used without further purification. − IR spectra were recorded on a Perkin−Elmer 1725 X FTIR spectrophotometer. − One- and two-dimensional ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on Bruker DPX 200 and DRX 400 NMR spectrometers. Spectra were referenced to external TMS (^{1}H and ^{13}C), $CFCl_3$ (^{19}F), and 85% H_3PO_4 (^{31}P). NMR samples were prepared by dissolving about 20 mg of the compound in 0.5 mL of deuterated solvent. Two-dimensional ^{1}H-NOESY and ^{19}F{^{1}H}-HOESY spectra were recorded with a mixing time of 500−800 ms. The assignment of all the resonances was achieved by a combination of ^{1}H-COSY, ^{1}H-NOESY, and "normal" and long-range ^{1}H-^{13}C HMQC experiments.

Synthesis of Complex 2a: Solid diacetyl bis(phenylimine) (131 mg, 0.55 mmol) and $NaBPh_4$ (large excess) were added to a solution of complex **1** (100 mg, 0.22 mmol) in methanol (10 mL). The resulting mixture was stirred and refluxed for 4 h, in the course of which its colour changed from yellow to deep-red. After cooling, the solution was placed in a refrigerator. A white solid precipitated after 15 h, which was filtered off. A red crystalline product precipitated from the remaining solution (10 mg, yield 5%). − $C_{49}H_{57}BN_2O_2P_2Ru$ (879.8): calcd. C 66.90, H 6.53, N 3.18; found C 66.96, H 6.72, N 3.21. − IR (CH_2Cl_2, 298 K): ν_{CO} = 1958 cm^{-1}, ν_{COMe} = 1625 cm^{-1}. − ^{1}H NMR ($CDCl_3$, 298 K, 400.13 MHz): δ = 1.20 (Harris t, $|^2J_{HP} + {}^4J_{HP}|$ = 7.2, PMe_3), 1.90 (t, $^5J_{HP}$ = 2.0, Me^d), 1.94 (t, $^5J_{HP}$ = 2.8, Me$^{d'}$), 2.18 (s, COMe), 6.60 (dd, $^3J_{HH}$ = 6.6, $^4J_{HH}$ = 1.8, $o^{a'}$), 6.69 (dd, $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 1.2, o^a), 6.88 (t, $^3J_{HH}$ = 7.2, *p*), 7.01 (t, $^3J_{HH}$ = 7.3, *m*), 7.41 (br, *o*), 7.45 (m, p^c and $p^{c'}$), 7.53 (m, $m^{b'}$ and m^b). − ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 100.55 MHz): δ = 15.5 (Harris t, $|^1J_{CP} + {}^3J_{CP}|$ = 30.1, PMe_3), 21.7 (s, Me^d), 23.2 (s, Me$^{d'}$), 51.3 (s, CO*Me*), 120.3 (s, $o^{a'}$), 121.5 (s, o^a), 122.1 (s, *p*), 125.9 (q, $^3J_{C11B}$ = 2.6, *m*), 128.5 (s, $p^{c'}$), 128.8 (s, p^c), 129.6 (s, $m^{b'}$), 130.5 (s, m^b), 136.7 (s, *o*), 149.28 (s, C_{ipso}−N), 149.29 (s, C_{ipso}−N), 164.5 (q, $^1J_{C11B}$ = 49.3, C_{ipso}), 173.4 (s, C=N), 176.0 (s, C=N), 204.3 (s, CO), 253.6 (s, *C*OMe). − ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K, 161.98 MHz): δ = −11.8 (s, PMe_3).

Synthesis of Complex 2b: Complex **1** (100 mg, 0.22 mmol) was dissolved in diethyl ether (5 mL). Solid $AgBF_4$ (41 mg, 0.21 mmol) was then added and the mixture was stirred for 24 h. The precipitate containing AgI and a solvento intermediate complex was collected by filtration, dried, and washed with a solution of diacetyl bis(phenylimine) (78.6 mg, 0.33 mmol) in CH_2Cl_2 (10 mL). The resulting solution was stirred for 4 h; *n*-hexane was then added until precipitation commenced. On placing the solution in a refrigerator at −18 °C, a red solid precipitated, which was collected by filtration, washed with *n*-hexane, and dried in vacuo (30 mg, yield 21%). − $C_{25}H_{37}BF_4N_2O_2P_2Ru$ (647.4): calcd. C 46.39, H 5.76, N 4.33; found C 46.58, H 5.80, N 4.12. − IR (CH_2Cl_2, 298 K): ν_{CO} = 1956 cm^{-1}, ν_{COMe} = 1623 cm^{-1}. − ^{1}H NMR (CD_2Cl_2, 298 K, 400.13 MHz): δ = 1.38 (Harris t, $|^2J_{HP} + {}^4J_{HP}|$ = 7.2, PMe_3), 2.23 (s, COMe), 2.43 (t, $^5J_{HP}$ = 2.7, Me$^{d'}$), 2.49 (t, $^5J_{HP}$ = 1.9, Me^d), 6.84 (dd, $^3J_{HH}$ = 8.4, $^4J_{HH}$ = 1.2, $o^{a'}$), 7.01 (dd, $^3J_{HH}$ = 8.2, $^4J_{HH}$ = 1.1, o^a), 7.46 (tt, $^3J_{HH}$ = 8.6, $^4J_{HH}$ = 1.1, m^c), 7.49 (tt, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.2, $m^{c'}$), 7.56 (t, $^3J_{HH}$ = 7.1, $m^{b'}$), 7.63 (t, $^3J_{HH}$ = 7.5, m^b). − ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K, 161.98 MHz): δ = −11.7 (s, PMe_3). − ^{19}F NMR (CD_2Cl_2, 298 K, 376.50 MHz): δ = −152.08 (br, $^{10}BF_4^-$), −152.13 (br, $^{11}BF_4^-$).

Synthesis of Complex 3: The procedure was the same as that used for complex **2b**. At the final stage, a mixture of complexes **3** and **4a** was obtained. Characterization of complex **3:** IR (CH_2Cl_2, 298 K): ν_{CO} = 1953 cm^{-1}, ν_{COMe} = 1641 cm^{-1}. − ^{1}H NMR (CD_2Cl_2, 298 K, 400.13 MHz): δ = 1.36 (Harris t, $|^2J_{HP} + {}^4J_{HP}|$ = 7.2, PMe_3), 2.26 (s, COMe), 2.46 (t, $^5J_{HP}$ = 2.8, Me$^{c'}$), 2.53 (t, $^5J_{HP}$ = 1.9, Me^c), 6.84 (dd, $^3J_{HH}$ = 9.0, $^4J_{HF}$ = 4.6, $o^{a'}$), 7.05 (dd, $^3J_{HH}$ = 9.0, $^4J_{HF}$ = 4.6, o^a), 7.27 (t, $^3J_{HH}$ = 9.0, $^3J_{HF}$ = 8.3, $m^{b'}$), 7.33 (t, $^3J_{HH}$ = 9.0, $^3J_{HF}$ = 8.2, m^b). − ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 100.55 MHz): δ = 15.5 (Harris t, $|^1J_{CP} + {}^3J_{CP}|$ = 30.1, PMe_3), 21.8 (s, Me$^{d'}$), 23.3 (s, Me^d), 50.8 (t, $^4J_{CP}$ = 1.6, CO*Me*), 115.9 (d, $^2J_{CF}$ = 28.2, $m^{b'}$), 117.2 (d, $^2J_{CF}$ = 30.6, m^b), 123.2 (d, $^3J_{CF}$ = 9.0, $o^{a'}$), 124.3 (d, $^3J_{CF}$ = 9.6, o^a), 145.4 (s, $p^{d'}$), 145.7 (s, p^d), 161.93 (d, $^1J_{CF}$ = 248.8, C_{ipso}−N), 161.94 (d, $^1J_{CF}$ = 246.6, C_{ipso}−N), 174.6 (s, C=N), 177.6 (s, C=N), 204.8 (t, $^2J_{CP}$ = 14.7, CO), 253.2 (t, $^2J_{CP}$ = 10.5, *C*OMe). − ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K, 161.98 MHz): δ = −11.6 (s, PMe_3). − ^{19}F NMR (CD_2Cl_2, 298 K, 376.50 MHz): δ = −114.2 (tt, $^3J_{FH}$ = 9.0, $^4J_{FH}$ = 8.0, $p^{d'}$), −115.5 (tt, $^3J_{FH}$ = 9.0, $^4J_{FH}$ = 8.0, p^d), −150.6 (br, $^{10}BF_4^-$), −150.7 (br, $^{11}BF_4^-$).

Synthesis of Complex 4a: The procedure was similar to that used for complex **2b**, but the precipitate was washed with neat dichloromethane free from any ligands (yield 30%). The coordinated water was probably present in the hygroscopic $AgBF_4$ salt. − $C_9H_{23}BF_4O_3P_2Ru$ (429.1): calcd. C 25.20, H 5.40; found C 25.36, H 5.45. − IR (CH_2Cl_2, 298 K): ν_{CO} = 1973, 2042 cm^{-1}. − ^{1}H NMR (CD_2Cl_2, 298 K, 400.13 MHz): δ = 0.08 (t, $^3J_{HP}$ = 7.9, Me), 1.57 (Harris t, $|^2J_{HP} + {}^4J_{HP}|$ = 7.4, PMe_3), 3.93 (s, H_2O). − ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 100.55 MHz): δ = −3.68 (s, Me), 15.0 (Harris t, $|^1J_{CP} + {}^3J_{CP}|$ = 31.7, PMe_3), 189.9 (s, CO), 201.0 (s, CO). − ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K, 161.98 MHz): δ = −3.21 (s, PMe_3). − ^{19}F NMR (CD_2Cl_2, 298 K, 376.50 MHz): δ = −149.8 (vbr, $^{10}BF_4^-$), −149.9 (br, $^{11}BF_4^-$).

Synthesis of Complex 4b: Solid $TlPF_6$ (73 mg, 0.21 mmol) was added to a solution of complex **1** (100 mg, 0.22 mmol) in methanol (5 mL). Immediately, TlI precipitated from the solution and was filtered off. The filtrate was treated with a large excess of solid $NaBPh_4$. After a few minutes, complex **4b** precipitated; it was collected by filtration, washed with cold methanol, and dried in vacuo (140 mg, yield 94%). − $C_{34}H_{45}BO_3P_2Ru$ (675.6): calcd. C 60.46, H 6.71; found C 60.54, H 6.78. − IR (CH_2Cl_2, 298 K): ν_{CO} = 1975, 2033 cm^{-1}. − ^{1}H NMR (CD_2Cl_2, 298 K, 400.13 MHz): δ = −0.85 (br, *Me*OH), −0.61 (t, $^3J_{HP}$ = 8.0, Me), 1.33 (Harris t, $|^2J_{HP} + {}^4J_{HP}|$ = 7.0, PMe_3), 3.45 (s, MeO*H*), 6.96 (t, $^3J_{HP}$ = 7.2, *p*), 7.10 (t, $^3J_{HP}$ = 7.4, *m*), 7.56 (br, *o*). − ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 100.55 MHz): δ = −6.98 (t, $^2J_{CP}$ = 9.3, Me), 15.6 (Harris t, $|^1J_{CP} + {}^3J_{CP}|$ = 31.7, PMe_3), 30.0 (s, MeOH), 122.8 (s, *p*), 126.6 (s, *m*), 136.1 (s, *o*), 165.0 (q, $^1J_{C11B}$ = 49.5, C_{ipso}), 190.5 (t, $^2J_{CP}$ = 8.6, CO), 199.5 (t, $^2J_{CP}$ = 13.5, CO). − ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K, 161.98 MHz): δ = −5.57 (s, PMe_3).

Synthesis of Complex 5: Ethylenediamine (22 μL, ca. 0.33 mmol) was added to a solution of complex **1** (100 mg, 0.22 mmol) in methanol (5 mL) and the solution was stirred for 10 min. A large excess of $NaBPh_4$ was then added, which resulted in the precipitation of a white solid. It was collected by filtration, washed with cold methanol, and dried in vacuo (130 mg, yield 85%). − $C_{35}H_{49}BN_2O_2P_2Ru$ (703.6): calcd. C 59.75, H 7.02, N 3.98; found C 59.28, H 6.50, N 3.25. − IR (CH_2Cl_2, 298 K): ν_{CO} = 1944 cm^{-1}, ν_{COMe} = 1614 cm^{-1}. − ^1H NMR (CD_2Cl_2, 298 K, 400.13 MHz): δ = 1.11 (br, NH_2^d), 1.33 (Harris t, $|^2J_{HP} + {}^4J_{HP}|$ = 6.3, PMe_3), 1.93 (m, $^2J_{HH}$ = 11.6, $^3J_{HH}$ = 6.0, CH_2^c), 2.18 (m, $^2J_{HH}$ = 11.7, $^3J_{HH}$ = 5.9, CH_2^b), 2.28 (s, COMe), 2.60 (br, NH_2^a), 6.94 (t, $^3J_{HH}$ = 6.1, *p*), 7.09 (t, $^3J_{HH}$ = 7.4, *m*), 7.41 (br, *o*). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 100.55 MHz): δ = 15.3 (Harris t, $|^1J_{CP} + {}^3J_{CP}|$ = 29.2, PMe_3), 43.6 (s, CH_2^c), 45.7 (s, CH_2^b), 48.0 (s, CO*Me*), 122.4 (s, *p*), 126.2 (s, *m*), 136.3 (s, *o*), 164.4 (q, $^1J_{C11B}$ = 49.3, C_{ipso}), 202.7 (t, $^2J_{CP}$ = 15.4, CO), 263.6 (t, $^2J_{CP}$ = 10.8, *C*OMe). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K, 161.98 MHz): δ = −6.71 (s, PMe_3).

Synthesis of Complex 6: The synthetic procedure was similar to that described for complex **5**. Yield: 60%. − $C_{37}H_{53}BN_2O_2P_2Ru$ (731.7): calcd. C 60.74, H 7.30, N 3.83; found C 59.32, H 7.16, N 3.73. − IR (CH_2Cl_2, 298 K): ν_{CO} = 1945 cm^{-1}, ν_{COMe} = 1603 cm^{-1}. − ^1H NMR (CD_2Cl_2, 298 K, 400.13 MHz): δ = 1.20 (t, $^3J_{HH}$ = 7.2, C*H*$_3$CH$_2$), 1.36 (dd, $^2J_{HP}$ = 7.8, $^4J_{HP}$ = 1.4, PMe_3^1), 1.39 (dd, $^2J_{HP}$ = 7.7, $^4J_{HP}$ = 1.5, PMe_3^2), 1.65 (br, NH^d), 1.71 (br, H^a), 1.77 (m, H^d), 2.34 (s, COMe), 2.43 (br. d, $^2J_{HH}$ = 15.9, H^c), 2.58 (m, H^b), 2.59 (m, NH_2^a and CH_3CH_2), 6.97 (t, $^3J_{HH}$ = 7.2, *p*), 7.10 (t, $^3J_{HH}$ = 7.4, *m*), 7.42 (br, *o*). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 100.55 MHz): δ = 15.2 (dd, $^1J_{CP}$ = 26.4, $^3J_{CP}$ = 2.9, PMe_3^1), 15.9 (s, *C*H$_3$CH$_2$), 16.9 (dd, $^1J_{CP}$ = 25.8, $^3J_{CP}$ = 3.1, PMe_3^2), 43.7 (s, C^c), 48.1 (s, CO*Me*), 50.4 (s, CH_3CH_2), 54.1 (s, C^b), 122.5 (s, *p*), 126.1 (s, *m*), 136.3 (s, *o*), 164.5 (q, $^1J_{C11B}$ = 49.3, C_{ipso}), 203.7 (t, $^2J_{CP}$ = 15.2, CO), 262.4 (t, $^2J_{CP}$ = 10.8, *C*OMe). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K, 161.98 MHz): δ = −10.78 (d, $^2J_{PP}$ = 254.9, $PMe_3^{1\text{ or }2}$), −6.74 (d, $^2J_{PP}$ = 254.9, $PMe_3^{2\text{ or }1}$).

Synthesis of Complex 7: The synthetic procedure was similar to that described for complex **5**. Yield: 95%. − $C_{38}H_{55}BN_2O_2P_2Ru$ (745.7): calcd. C 61.21, H 7.43, N 3.76; found C 61.27, H 7.33, N 3.30. − IR (CH_2Cl_2, 298 K): ν_{CO} = 1944 cm^{-1}, ν_{COMe} = 1599 cm^{-1}. − ^1H NMR (CD_2Cl_2, 298 K, 400.13 MHz): δ = 1.18 (d, $^3J_{HH}$ = 6.2, CH*Me*$_2$), 1.29 (d, $^3J_{HH}$ = 6.5, CH*Me*$_2$), 1.38 (d, $^2J_{HP}$ = 8.3, PMe_3^1), 1.40 (d, $^2J_{HP}$ = 8.0, PMe_3^2), 1.44 (br, NH^d), 1.79 (m, $H^{c\text{ or }c'}$ and $H^{b\text{ or }b'}$), 2.35 (s, COMe), 2.51 (br, $H^{c\text{ or }c'}$ and $NH^{a\text{ and }a'}$), 2.66 (m, CH), 2.75 (br, $H^{b\text{ or }b'}$ and $H^{c\text{ or }c'}$), 6.95 (t, $^3J_{HH}$ = 7.2, *p*), 7.10 (t, $^3J_{HH}$ = 7.4, *m*), 7.42 (br, *o*). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 100.55 MHz): δ = 15.3 (dd, $^1J_{CP}$ = 25.4, $^3J_{CP}$ = 3.8, PMe_3^1), 16.8 (dd, $^1J_{CP}$ = 25.2, $^3J_{CP}$ = 3.8, PMe_3^2), 22.0 (s, Me), 26.3 (s, Me), 44.2 (s, $CH_2^{b\text{ or }c}$), 47.6 (s, CO*Me*), 51.4 (s, $CH_2^{c\text{ or }b}$), 54.3 (s, CH), 122.3 (s, *p*), 126.3 (s, *m*), 136.2 (s, *o*), 164.3 (q, $^1J_{C11B}$ = 49.3, C_{ipso}), 203.9 (t, $^2J_{CP}$ = 15.2, CO), 260.2 (t, $^2J_{CP}$ = 10.6, *C*OMe). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K, 161.98 MHz): δ = −10.4 (d, $^2J_{PP}$ = 254.2, $PMe_3^{1\text{ or }2}$), −7.4 (d, $^2J_{PP}$ = 254.2, $PMe_3^{2\text{ or }1}$).

Synthesis of Complex 8: The procedure used was similar to that described for complex **5**. Yield: 65%. − $C_{37}H_{53}BN_2O_2P_2Ru$ (731.7): calcd. C 60.74, H 7.30, N 3.83; found C 60.22, H 7.11, N 3.70. − IR (CH_2Cl_2, 298 K): ν_{CO} = 1945 cm^{-1}, ν_{COMe} = 1592 cm^{-1}. − ^1H NMR (CD_2Cl_2, 298 K, 400.13 MHz): δ = 1.35 (dd, $^2J_{HP}$ = 8.3, $^4J_{HP}$ = 1.8, PMe_3^{1A}), 1.39 (dd, $^2J_{HP}$ = 8.1, $^4J_{HP}$ = 1.7, PMe_3^{1B}), 1.45 (dd, $^2J_{HP}$ = 7.7, $^4J_{HP}$ = 1.7, PMe_3^{2B}), 1.53 (dd, $^2J_{HP}$ = 7.5, $^4J_{HP}$ = 1.8, PMe_3^{2A}), 1.78 (br, $H^{b\text{ or }b'B}$), 1.80 (br, NH^{dB}), 1.82 (br, $H^{b'\text{ or }bB}$), 1.96 (NH^{dA}), 2.15 (br, $H^{c'A}$), 2.21 (br, H^{bA}), 2.29 (br, $H^{b'A}$), 2.35 (s, $COMe^A$), 2.37 (s, $COMe^B$), 2.39 (br, H^{cB}), 2.41 (br, H^{cA}), 2.44 (d, $^3J_{HH}$ = 6.5, Me^{dB}), 2.46 (d, $^3J_{HH}$ = 6.2, $Me^{d'A}$), 2.53 (d, $^2J_{HH}$ = 6.2, $Me^{a'B}$), 2.54 (d, $^2J_{HH}$ = 6.2, $Me^{a'A}$), 2.67 (m, H^{cB}), 2.93 (br, NH^{aB}), 3.09 (br, NH^{aA}), 6.91 (t, $^3J_{HH}$ = 7.2, *p*), 7.08 (t, $^3J_{HH}$ = 7.4, *m*), 7.39 (br, *o*). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 100.55 MHz): δ = 14.4 (dd, $^1J_{CP}$ = 28.2, $^3J_{CP}$ = 1.8, PMe_3^{1A}), 16.0 (dd, $^1J_{CP}$ = 29.1, $^3J_{CP}$ = 2.5, PMe_3^{1B}), 17.6 (dd, $^1J_{CP}$ = 26.2, $^3J_{CP}$ = 2.8, PMe_3^{2B}), 18.8 (dd, $^1J_{CP}$ = 25.7, $^3J_{CP}$ = 2.6, PMe_3^{2A}), 42.3 (s, $Me^{d'B}$), 42.7 (br, $Me^{a'A}$, $Me^{d'A}$, and $Me^{a'B}$), 48.9 (s, CO*Me*^{A}), 49.1 (s, CO*Me*^{B}), 52.6 (s, C^{cA}), 54.0 (s, C^{bA}), 54.4 (s, C^{bB}), 54.5 (s, C^{cB}), 122.1 (s, *p*), 126.0 (s, *m*), 136.3 (s, *o*), 164.4 (q, $^1J_{C11B}$ = 49.3, C_{ipso}), 203.3 (s, CO^A), 263.1 (s, *C*OMe^A). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K, 161.98 MHz): δ = −3.83 (d, $^2J_{PP}$ = 256.1, $PMe_3^{1\text{ or }2A}$), −7.37 (d, $^2J_{PP}$ = 256.2, $PMe_3^{1\text{ or }2B}$), −13.4 (d, $^2J_{PP}$ = 256.1, $PMe_3^{2\text{ or }1B}$), −20.3 (d, $^2J_{PP}$ = 256.1, $PMe_3^{2\text{ or }1A}$).

Synthesis of Complex 9: (a) The procedure used was similar to that described for complex **5**. The reaction required 2 days and gave a 12% yield of **9**. (b) Solid $TlPF_6$ (73 mg, 0.21 mmol) was added to a solution of complex **1** (100 mg, 0.22 mmol) in methanol (5 mL). Immediately, TlI was precipitated, which was filtered off. The filtrate was treated with liquid *N*,*N*′-dibenzylethylenediamine (0.11 mL, 0.44 mmol) and solid $NaBPh_4$ (large excess). After 2 h, complex **9** precipitated; it was collected by filtration, washed with cold methanol, and dried in vacuo (60 mg, yield 30%). − $C_{49}H_{61}BN_2O_2P_2Ru$ (883.9): calcd. C 66.59, H 6.96, N 3.17; found C 65.21, H 6.72, N 3.10. − IR (CH_2Cl_2, 298 K): ν_{CO} = 1947 cm^{-1}, ν_{COMe} = 1608 cm^{-1}. − ^1H NMR (CD_2Cl_2, 298 K, 400.13 MHz): δ = 1.33 (dd, $^2J_{HP}$ = 7.5, $^4J_{HP}$ = 1.8, PMe^{1A} and PMe^{1B}), 1.47 (dd, $^2J_{HP}$ = 8.1, $^4J_{HP}$ = 1.8, PMe^{2B}), 1.69 (dd, $^2J_{HP}$ = 7.5, $^4J_{HP}$ = 1.8, PMe^{2A}), 1.90 (br, H^{dB}), 1.95 (br, $H^{c'A}$), 2.29 (br, H^{dA}), 2.42 (s, CO*Me*^{B}), 2.46 (s, CO*Me*^{A}), 2.61 (br, $H^{c'B}$), 2.67 (d, $H^{b'B}$), 2.71 (d, H^{bB}), 2.75 (br, $H^{b'A}$), 2.79 (br, $H^{c'A}$), 2.89 (t, $^2J_{HH}$ = 11.6, $H^{bz(I)B}$), 3.2 (br, H^{aB}), 3.35 (t, $^2J_{HH}$ = 12.0, $H^{bz(I)A}$), 3.36 (br, H^{aA}), 3.66 (br, H^{bzA}), 3.70 (H^{bzB} and H^{bzB}), 3.71 (br, H^{cB}), 3.97 (dd, $^1J_{HH}$ = 13.0, $^3J_{HH}$ = 5.1, H^{bzA}), 4.26 (d, $^1J_{HH}$ = 12.1, $H^{bz(I)A}$), 4.50 (br, $H^{bz(I)B}$), 6.90 (tt, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 1.2, *p*), 7.04 (t, $^3J_{HH}$ = 7.4, *m*), 7.26 (m, o^A), 7.33 (m, o^B), 7.37 (m, *o*), 7.489 (m, m^A), 7.492 (m, $o^{(I)B}$), 7.505 (m, m^B), 7.54 (m, $o^{(I)A}$). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 100.55 MHz): δ = 14.0 (dd, $^1J_{CP}$ = 28.3, $^3J_{CP}$ = 1.8, PMe_3^{1A}), 15.4 (dd, $^1J_{CP}$ = 27.0, $^3J_{CP}$ = 2.3, PMe_3^{2B}), 17.4 (dd, $^1J_{CP}$ = 26.5, $^3J_{CP}$ = 2.7, PMe_3^{1B}), 19.1 (dd, $^1J_{CP}$ = 26.0, $^3J_{CP}$ = 2.5, PMe_3^{2A}), 47.6 (s, CH_2^{cA}), 48.24, 48.27, and 48.30 (s, CO*Me*^{B}), 48.52 and 48.54 (s, CO*Me*^{A}), 50.0 (s, CH_2^{bA}), 50.8 (s, CH_2^{bB}), 53.8 (s, CH_2^{cB}), 56.9 (dd, $^3J_{CP}$ = 6.8, $^3J_{CP}$ = 2.5, $CH_2^{bz(I)A}$), 59.3 (s, CH_2^{bzB}), 59.7 (s, $CH_2^{bz(I)B}$), 60.0 (s, CH_2^{bzA}), 121.9 (s, *p*), 125.7 (m, *m*), 128.8 (s, o^A), 129.3 (s, $o^{(I)A}$), 129.6 (s, o^B), 129.7 (s, $o^{(I)b}$), 136.1 (m, *o*), 164.4 (q, $^1J_{C11B}$ = 49.0, C_{ipso}), 202.9 (t, $^2J_{CP}$ = 15.8, CO^A), 203.4 (t, $^2J_{CP}$ = 15.8, CO^B), 261.8 (t, $^2J_{CP}$ = 11.6, *C*OMe^B), 262.8 (t, $^2J_{CP}$ = 10.1, *C*OMe^A). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K, 161.98 MHz): δ = −4.3 (d, $^2J_{PP}$ = 249, $PMe_3^{2\text{ or }1A}$), −5.7 (d, $^2J_{PP}$ = 256, $PMe_3^{2\text{ or }1B}$), −13.8 (d, $^2J_{PP}$ = 256, $PMe_3^{1\text{ or }2B}$), −20.2 (d, $^2J_{PP}$ = 249, $PMe_3^{1\text{ or }2A}$).

Synthesis of Complex 10: The procedure used was similar to that described for complex **5**. Yield: 27%. − $C_{37}H_{53}BN_2O_2P_2Ru$ (731.7): calcd. C 60.74, H 7.30, N 3.83; found C 60.13, H 7.32, N 3.86. − IR (CH_2Cl_2, 298 K): ν_{CO} = 2039 cm^{-1}, ν_{COMe} = 1950 cm^{-1}. − ^1H NMR (CD_2Cl_2, 298 K, 400.13 MHz): δ = −0.27 (t, $^3J_{HP}$ = 8.0, Me), 1.55 (Harris t, $|^2J_{HP} + {}^4J_{HP}|$ = 6.9, PMe_3), 2.29 (s, Me_2N), 2.32 (br, CH_2^{α}, NH_2), 2.54 (br, CH_2^{β}), 6.93 (t, $^3J_{HH}$ = 7.2, *p*), 7.08 (t, $^3J_{HH}$ = 7.4, *m*), 7.37 (br, *o*). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 100.55 MHz): δ = −7.13 (t, $^2J_{CP}$ = 9.4, Me), 15.9 (Harris t, $|^1J_{CP} + {}^3J_{CP}|$ = 31.9, PMe_3), 45.5 (s, Me_2N), 48.7 (s, CH_2^{β}), 59.7 (s,

CH_2^{α}), 122.1 (s, *p*), 126.0 (s, *m*), 136.3 (s, *o*), 164.7 (q, $^1J_{C11B}$ = 48.9, C_{ipso}), 191.3 (t, $^2J_{CP}$ = 8.4, CO), 199.3 (s, $^2J_{CP}$ = 13.5, CO). – $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K, 161.98 MHz): δ = 6.87 (s, PMe_3).

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