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Ruthenium(II) and ruthenium(IV) complexes containing hemilabile heterodifunctional iminophosphorane-phosphine ligands $Ph_2PCH_2P(=NR)Ph_2$ †

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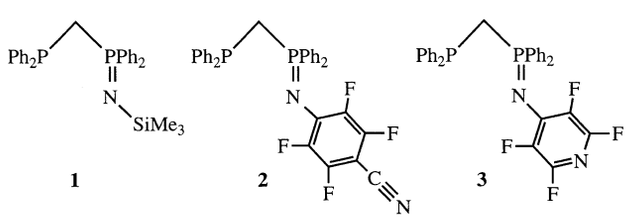
The dimeric complex [{Ru(η⁶-*p*-cymene)(μ-Cl)Cl}$_2$] reacts with iminophosphorane-phosphine ligands Ph_2PCH_2-P(=NR)Ph_2 (R = $SiMe_3$ **1**, *p*-C_6F_4CN **2**, *p*-C_5F_4N **3**), in dichloromethane at room temperature, to afford the neutral derivatives [Ru(η⁶-*p*-cymene)Cl_2{κ¹-*P*-$Ph_2PCH_2P(=NR)Ph_2$}] (R = $SiMe_3$ **4**, *p*-C_6F_4CN **5**, *p*-C_5F_4N **6**). Treatment of **4**–**6** with $NaPF_6$ in methanol allows the preparation of cationic species [Ru(η⁶-*p*-cymene)Cl{κ²-*P,N*-$Ph_2PCH_2P(=NR)$-Ph_2}][PF_6] (R = H **7**, *p*-C_6F_4CN **8**, *p*-C_5F_4N **9**). While complexes **8** and **9** react with anionic ligands yielding neutral derivatives [Ru(η⁶-*p*-cymene)X_2{κ¹-*P*-$Ph_2PCH_2P(=NR)Ph_2$}] (R = *p*-C_6F_4CN, X = Br **10a**, I **10b**, N_3 **10c**, CN **10d**, NCO **10e**; R = *p*-C_5F_4N, X = Br **11a**, I **11b**, N_3 **11c**, CN **11d**, NCO **11e**), cationic species [Ru(η⁶-*p*-cymene)X{κ²-*P,N*-$Ph_2PCH_2P(=NH)Ph_2$}][PF_6] (X = Br **12a**, I **12b**, N_3 **12c**, CN **12d**, NCO **12e**) are exclusively formed starting from **7**. Complexes **8** and **9** also react with neutral ligands such as phosphines, pyridine, acetonitrile or isocyanides affording compounds [Ru(η⁶-*p*-cymene)Cl(PR_3){κ¹-*P*-$Ph_2PCH_2P(=NR)Ph_2$}][PF_6] (R = *p*-C_6F_4CN, PR_3 = PMe_3 **13a**, PMe_2Ph **13b**, $PMePh_2$ **13c**, PPh_3 **13d**; R = *p*-C_5F_4N, PR_3 = PMe_3 **14a**, PMe_2Ph **14b**, $PMePh_2$ **14c**, PPh_3 **14d**), [Ru(η⁶-*p*-cymene)Cl(py){κ¹-*P*-$Ph_2PCH_2P(=NR)Ph_2$}][PF_6] (R = *p*-C_6F_4CN **15**; R = *p*-C_5F_4N **16**), [Ru(η⁶-*p*-cymene)Cl-(N≡CMe){κ¹-*P*-$Ph_2PCH_2P(=NR)Ph_2$}][PF_6] (R = *p*-C_6F_4CN **17**; R = *p*-C_5F_4N **18**) and [Ru(η⁶-*p*-cymene)Cl(CNR′)-{κ¹-*P*-$Ph_2PCH_2P(=NR)Ph_2$}][PF_6] (R = *p*-C_6F_4CN, R′ = Cy **19a**, 2,6-$C_6H_3Me_2$ **19b**; R = *p*-C_5F_4N, R′ = Cy **20a**, 2,6-$C_6H_3Me_2$ **20b**), respectively. The synthesis of complexes [Ru(η³:η³-$C_{10}H_{16}$)Cl_2{κ¹-*P*-$Ph_2PCH_2P(=NR)Ph_2$}] (R = $SiMe_3$ **21**, *p*-C_6F_4CN **22**, *p*-C_5F_4N **23**) and [Ru(η³:η³-$C_{10}H_{16}$)Cl{κ₂-*P,N*-$Ph_2PCH_2P(=NH)Ph_2$}][BF_4] **24** starting from the bis(allyl)-ruthenium(IV) dimer [{Ru(η³:η³-$C_{10}H_{16}$)(μ-Cl)Cl}$_2$] and ligands **1**–**3** is also reported.

The coordination chemistry of heterodifunctional ligands, bearing both "hard" (*e.g.* N, O) and "soft" (*e.g.* P) donor atoms, is an area of considerable current interest since they show hemilabile[1] properties providing potential applications in catalysis.[2] Typical examples are the well-known diphosphine-monoxides, *e.g.* R_2P–$(CH_2)_n$–P(=O)R_2, which, since the pioneering works by Grim and co-workers,[3] have been widely studied and successfully applied in a large number of catalytic transformations.[4] In contrast, much less attention has been devoted to the chemistry of the closely related iminophosphorane-phosphine ligands R_2P–$(CH_2)_n$–P(=NR′)R_2,[5] although they are readily accessible from diphosphines *via* selective monoimination with a large variety of azides (Staudinger reaction).[6,7] Most of the reported complexes belong to the series of the functionalized dppm ligands Ph_2P–CH_2–P(=NR)Ph_2, *i.e.* Ni,[8] Pd,[6c,6f,9] Mo,[10] W,[10a] Co,[8a] Rh,[8a,9d,10a,11] Ir,[10a,11d] Ti,[6b,12] and Re[13] species, in which the iminophosphorane-phosphines are acting as chelate ligands through the P(III) and N atoms. Although some of them show catalytic activity in hydrogenation of olefins,[11c] and carbonylation of methanol,[8a] as far as we are aware, no studies on their hemilabile properties have been reported to date.

Following our interest in the chemistry of ruthenium complexes containing hybrid P/N-donor ligands,[14] here we describe the preparation of the first ruthenium(II) and ruthenium(IV) complexes containing iminophosphorane-phosphine ligands (see Chart 1). In addition, the lability of the coordinated –Ph_2P=NR moiety in some of these complexes has been investigated.



1 **2** **3**

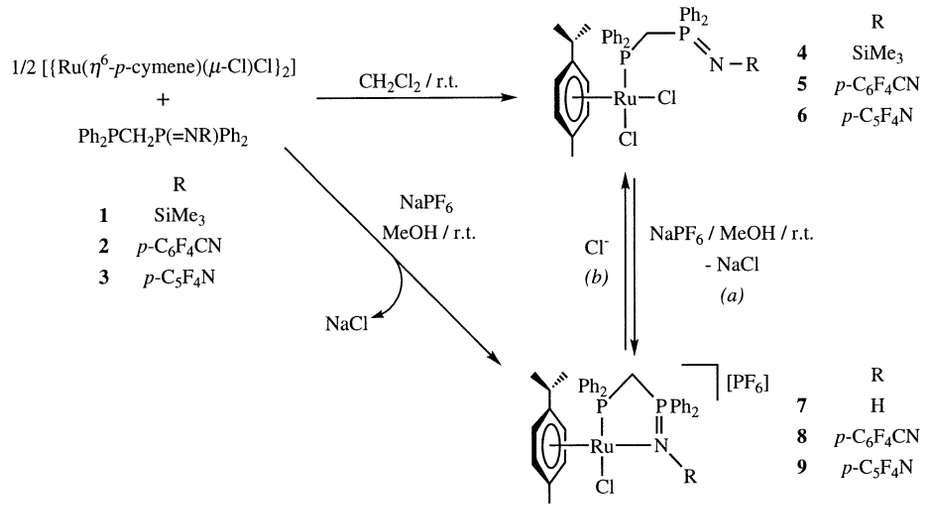
Chart 1 Iminophosphorane-phosphine ligands used in this paper.

Results and discussion

Synthesis of ruthenium(II) complexes [Ru(η⁶-*p*-cymene)Cl_2{κ¹-*P*-$Ph_2PCH_2P(=NR)Ph_2$}] (R = $SiMe_3$ **4**, *p*-C_6F_4CN **5**, *p*-C_5F_4N **6**) and [Ru(η⁶-*p*-cymene)Cl{κ²-*P,N*-$Ph_2PCH_2P(=NR)Ph_2$}][PF_6] (R = H **7**, *p*-C_6F_4CN **8**, *p*-C_5F_4N **9**)

The ability of dimers [{Ru(η⁶-arene)(μ-Cl)Cl}$_2$] to form mono- and dinuclear ruthenium(II) complexes of general formula [Ru-(η⁶-arene)Cl_2L] and [{Ru(η⁶-arene)Cl_2}$_2$(μ-L)] is well-known.[15] As expected, we have found that the reaction of [{Ru(η⁶-*p*-cymene)(μ-Cl)Cl}$_2$][16] with a two-fold excess of iminophosphorane-phosphines $Ph_2PCH_2P(=NR)Ph_2$ (R = $SiMe_3$ **1**,

† Electronic supplementary information (ESI) available: analytical and spectroscopic data. See http://www.rsc.org/suppdata/dt/b1/b110442j/



Scheme 1 Coordination of iminophosphorane-phosphine ligands on a (η^6-arene)-ruthenium(II) moiety: (a) Molar ratio complex/$NaPF_6$: **4** (1 : 1), **5** (1 : 12), **6** (1 : 12). (b) R = *p*-C_6F_4CN, *p*-C_5F_4N.

p-C_6F_4CN **2**, *p*-C_5F_4N **3**),[6b,10a] in dichloromethane at room temperature, affords the mononuclear compounds [Ru(η^6-*p*-cymene)Cl_2\{κ^1-*P*-Ph_2PCH_2P(=NR)Ph_2\}] (R = $SiMe_3$ **4**, *p*-C_6F_4CN **5**, *p*-C_5F_4N **6**; 69–78% yield) (Scheme 1). No dinuclear bridged products were detected even when the reactions were carried out with only one equivalent of Ph_2PCH_2P(=NR)Ph_2 obtaining instead equimolar mixtures of **4**–**6** and the precursor complex [{Ru(η^6-*p*-cymene)(μ-Cl)Cl}$_2$].

The unequivocal characterization of complexes **4**–**6** was achieved by means of standard spectroscopic techniques (IR and ^{31}P-{^{1}H}, ^{1}H, ^{19}F and ^{13}C-{^{1}H}) as well as elemental analyses (see Tables S1–S4 provided as Supplementary Information †). The most significant features are: (i) (^{31}P-{^{1}H} NMR) Two doublet resonances (^2J(PP) = 35.1–37.4) consistent with an AX spin system in the ranges δ_P −5.8 to 9.2 and 21.5–22.0 corresponding to the iminophosphorane and phosphine moieties, respectively. (ii) (^{1}H NMR) A virtual triplet signal (^2J(HP) = 8.8–10.3 Hz) at 3.75–4.28 ppm for the methylenic PCH_2P protons. (iii) (^{13}C-{^{1}H} NMR) A doublet of doublets resonance (J(CP) = 55.3–76.3 (P(v)) and 18.0–25.0 (P(III))) for the PCH_2P carbon at *ca.* 22 ppm. And, (iv) (^{19}F NMR) the presence for complexes **5** and **6** of two multiplets (AA′BB′ spin system) at similar chemical shifts (see Tables S1 and S3 provided as Supplementary Information †) to those reported for the free ligands **2** and **3**.[10a] IR absorption bands which appear in the range of 1000–1300 cm^{-1} can be tentatively assigned to ν(P=N) of the iminophosphorane group, but they are in general overlapped by those of the rest of the ligands, and consequently, the correct assignment is uncertain.

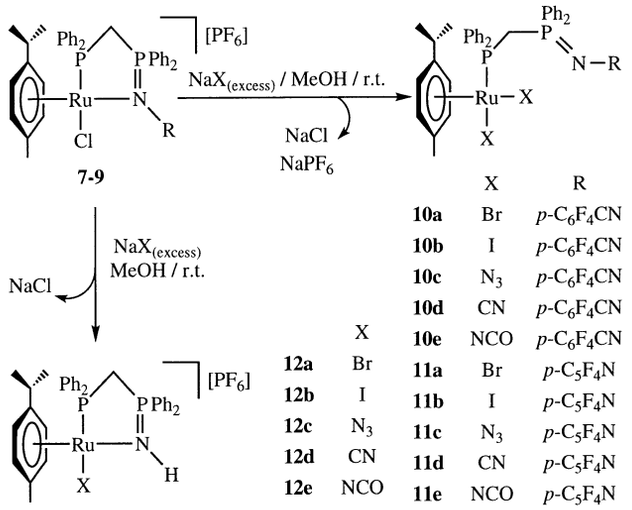
Treatment of [Ru(η^6-*p*-cymene)Cl_2\{κ^1-*P*-Ph_2PCH_2P(=NR)Ph_2\}] (R = $SiMe_3$ **4**, *p*-C_6F_4CN **5**, *p*-C_5F_4N **6**) with $NaPF_6$, in methanol at room temperature, allows the N-coordination of the iminophosphorane moiety to ruthenium affording cationic derivatives [Ru(η^6-*p*-cymene)Cl\{κ^2-*P*,*N*-Ph_2PCH_2P(=NR)Ph_2\}]-[PF_6] (R = H **7**, *p*-C_6F_4CN **8**, *p*-C_5F_4N **9**) in 79–84% yield (Scheme 1). Formation of complex **7** involves the desilylation of the coordinated Ph_2PCH_2P(=N$SiMe_3$)Ph_2 ligand in **4**. We note that the selective cleavage of the N–Si bond in the free ligand with methanol has been reported to produce Ph_2PCH_2P(=NH)Ph_2 and Me_3SiOMe.[17] In contrast to the formation of complex **7** which requires only one equiv. of $NaPF_6$, compounds **8** and **9** are only formed in the presence of a large excess of $NaPF_6$ (*ca.* 12 equiv.), otherwise a mixture containing the starting materials is obtained. This seems to indicate the existence of an equilibrium due to the presence of the chloride anion in the reaction mixture. In fact the reversible process occurs when **8**–**9** are treated with an excess of NaCl in methanol affording the precursor complexes **5**–**6** in almost quantitative yields (Scheme 1). Complexes **7**–**9** can be also prepared in similar yields starting from [{Ru(η^6-*p*-cymene)(μ-Cl)Cl}$_2$] by reaction with the corresponding iminophosphorane-phosphine and $NaPF_6$ in methanol at room temperature (Scheme 1).

Analytical and spectroscopic data (IR and ^{31}P-{^{1}H}, ^{1}H, ^{19}F and ^{13}C-{^{1}H}) for **7**–**9** are in agreement with the formation of a chelate ring (see Tables S5 and S6 provided as Supplementary Information †). This can be assessed spectroscopically by: (i) a strong downfield shift of the ^{31}P-{^{1}H} NMR signals with doublets (^2J(PP) = 15.5–22.0) in the ranges δ_P 48.3–50.0 (Ph_2P) and 54.5–55.3 (Ph_2P=N), as well as a slight deshielding (*ca.* $\Delta\delta_C$ = 7 ppm) of the methylenic PCH_2P carbon resonances (dd, J(CP) = 77.3–84.2 (P(v)) and 19.1–25.7 (P(III))), compared to the starting materials **4**–**6**. (ii) The chemical inequivalence of the methylenic PCH_2P protons which appear as one or two unresolved multiplets at 3.20–4.04 ppm. And, (iii) the inequivalence of the methyl and CH carbons and protons of the *p*-cymene group, as a consequence of the chirality of the ruthenium atom. A similar effect is also observed in the ^{19}F NMR spectra of complexes **8** and **9** which show, in addition to the expected PF_6^- doublet, four multiplets for the *p*-C_6F_4CN and *p*-C_5F_4N groups (see the Supplementary Information †). We also note that, although in the ^{1}H NMR spectrum of complex **7** the NH proton could not be detected, the presence of such functionality was clearly evidenced by the IR spectrum (KBr) which shows a ν(NH) absorption at 3367 cm^{-1}.

Hemilabile properties of ruthenium(II) complexes [Ru(η^6-*p*-cymene)Cl\{κ^2-*P*,*N*-Ph_2PCH_2P(=NR)Ph_2\}][PF_6] (R = H **7**, *p*-C_6F_4CN **8**, *p*-C_5F_4N **9**)

Taking into account the lability of the iminophosphorane-phosphines **2**–**3** in complexes **8**–**9** which allows the coordination of a chloride ligand through the decoordination of the –Ph_2P=NR moiety (Scheme 1), we believed the study of the scope of this reactivity in the presence of other anionic and neutral ligands to be of interest.

(a) Synthesis of [Ru(η^6-*p*-cymene)X_2\{κ^1-*P*-Ph_2PCH_2P(=NR)Ph_2\}] (R = *p*-C_6F_4CN, X = Br 10a, I 10b, N_3 10c, CN 10d, NCO 10e; R = *p*-C_5F_4N, X = Br 11a, I 11b, N_3 11c, CN 11d, NCO 11e) and [Ru(η^6-*p*-cymene)X\{κ^2-*P*,*N*-Ph_2PCH_2P(=NH)Ph_2\}]-[PF_6] (X = Br 12a, I 12b, N_3 12c, CN 12d, NCO 12e). Complexes **8** and **9** react with an excess (*ca.* 16 equiv.) of sodium salts NaX (X^- = Br^-, I^-, N_3^-, CN^-, NCO^-), in methanol at room temperature, to yield neutral derivatives [Ru(η^6-*p*-cymene)X_2\{κ^1-*P*-Ph_2PCH_2P(=NR)Ph_2\}] (R = *p*-C_6F_4CN, X = Br **10a**, I **10b**, N_3 **10c**, CN **10d**, NCO **10e**; R = *p*-C_5F_4N, X =



	X	R
10a	Br	*p*-C_6F_4CN
10b	I	*p*-C_6F_4CN
10c	N_3	*p*-C_6F_4CN
10d	CN	*p*-C_6F_4CN
10e	NCO	*p*-C_6F_4CN
11a	Br	*p*-C_5F_4N
11b	I	*p*-C_5F_4N
11c	N_3	*p*-C_5F_4N
11d	CN	*p*-C_5F_4N
11e	NCO	*p*-C_5F_4N

	X
12a	Br
12b	I
12c	N_3
12d	CN
12e	NCO

Scheme 2 Reactivity of complexes **7**–**9** towards anionic ligands.

Br **11a**, I **11b**, N_3 **11c**, CN **11d**, NCO **11e**) (69–92% yield; Scheme 2).

NMR spectroscopic data (see Tables S1–S4 provided as Supplementary Information †) provide structural information on the chelate ring opening. Thus, the monodentate coordination of the iminophosphorane-phosphine ligands is assessed in the $^{31}P-\{^1H\}$ NMR spectra by a lowfield shift in both Ph_2P (δ_P 15.1–39.0) and $Ph_2P{=}N$ (δ_P 8.2–10.2) resonances with respect to the parent compounds **8** and **9**, being comparable to those observed in monodentated complexes **5** and **6**. ^1H, $^{13}C-\{^1H\}$ and ^{19}F NMR spectra are also in accord with the proposed formulations (see Tables S1–S4 provided as Supplementary Information †), in particular the methylenic PCH_2P proton and carbon resonances which appear at 3.77–4.80 (vt, ^2J(HP) = 9.0–10.5) and 21.66–31.80 (dd, J(CP) = 51.1–72.7 (P(V)) and 12.4–25.0 (P(III))) ppm, respectively. Moreover, the structure of complex **10e** has been confirmed by a X-ray diffraction study. A drawing of the molecular structure is shown in Fig. 1; selected bond distances and angles are listed in the caption. The molecule exhibits an usual pseudooctahedral three-legged piano-stool geometry with values of the interligand angles N(1)–Ru–N(2), N(1)–Ru–P(1) and N(2)–Ru–P(1), and those between the centroid of the arene ring C* and the legs typical of a pseudo-octahedron. The two cyanate ligands are bound to ruthenium in a nearly linear fashion (Ru–N(1)–C(11) 176.9(5)°, N(1)–C(11)–O(1) 178.0(8)°, Ru–N(2)–C(12) 166.2(5)°, N(2)–C(12)–O(2) 178.6(9)°) showing bond lengths of Ru–N(1) 2.075(4) Å, N(1)–C(11) 1.127(7) Å, C(11)–O(1) 1.199(7) Å, Ru–N(2) 2.104(4) Å, N(2)–C(12) 1.116(7) Å and C(12)–O(2) 1.216(8) Å. It is worth mentioning that in transition-metal cyanato compounds a decision between N- and O-bonding from X-ray structural analysis is not so straightforward because of the very similar sizes and scattering factors for N and O.[18] We decided in favor of N-bonding on the basis of the following considerations: (i) Both N- and O-bonded models were refined to convergence, and the former gave significantly lower residuals (R = 0.0637 and R_w = 0.0708 as against R = 0.0652 and R_w = 0.0723). (ii) The virtual linearity of the Ru–N–C–O chains is more consistent with the N-bonded model.[19] The N-coordination is also enterely in accord with both molecular orbital calculations reported by Tuan and Hoffmann, which predict the greater stability of the M–NCO linkage.[20] Literature precedents for the O-coordination of the cyanate ion are scarce.[21] The structural parameters observed for the uncoordinated iminophosphorane unit (P(2)–N(3) 1.569(4) Å; C(13)–P(2)–N(3) 117.7(2)°, P(2)–N(3)–C(26) 139.0(4)°) can be compared with those reported in the literature for free R–P=N–R′ compounds.[22]

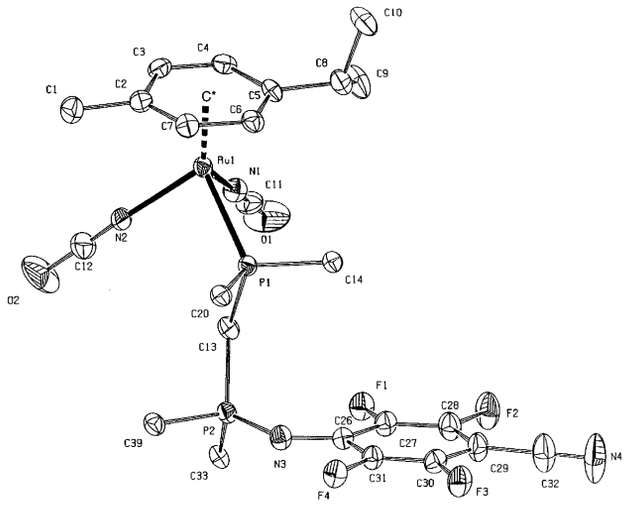


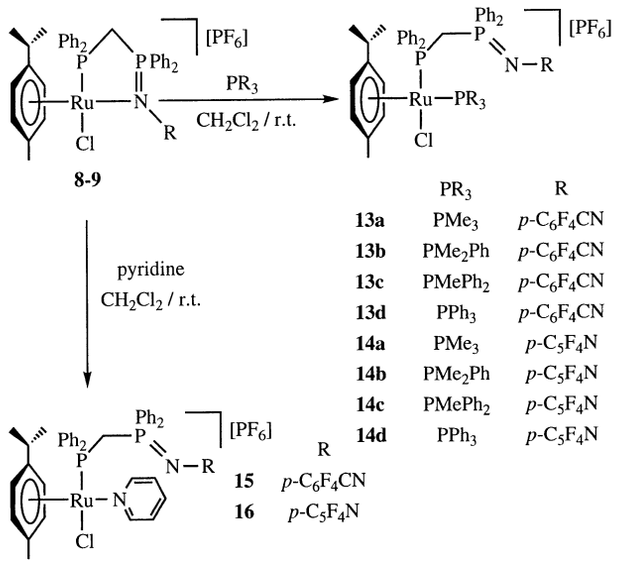
Fig. 1 ORTEP-type view of the structure of [Ru(η⁶-*p*-cymene)(κ¹-*N*-NCO)$_2${κ¹-*P*-Ph_2PCH_2P(=N-*p*-C_6F_4CN)Ph_2}] **10e** showing the crystallographic labeling scheme. Hydrogen atoms are omitted for clarity, and only the *ipso*-carbons of the phenyl rings are shown. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): Ru–C* 1.712(4); Ru–N(1) 2.075(4); Ru–N(2) 2.104(4); Ru–P(1) 2.340(1); N(1)–C(11) 1.127(7); N(2)–C(12) 1.116(7); C(11)–O(1) 1.199(7); C(12)–O(2) 1.216(8); P(1)–C(13) 1.842(5); C(13)–P(2) 1.828(5); P(2)–N(3) 1.569(4); N(3)–C(26) 1.333(6); C*–Ru–N(1) 129.0(2); C*–Ru–N(2) 127.4(2); C*–Ru–P(1) 129.3(2); Ru–N(1)–C(11) 176.9(5); Ru–N(2)–C(12) 166.2(5); Ru–P(1)–C(13) 111.28(16); Ru–P(1)–C(14) 111.64(16); Ru–P(1)–C(20) 114.13(16); N(1)–C(11)–O(1) 178.0(8); N(2)–C(12)–O(2) 178.6(9); N(1)–Ru–N(2) 84.78(17); N(1)–Ru–P(1) 84.27(12); N(2)–Ru–P(1) 86.60(12); P(1)–C(13)–P(2) 120.4(3); C(13)–P(2)–N(3) 117.7(2); P(2)–N(3)–C(26) 139.0(4); C(13)–P(2)–C(33) 104.8(2); C(13)–P(2)–C(39) 106.4(2). C* = centroid of the *p*-cymene ring (C(2), C(3), C(4), C(5), C(6), C(7)).

In contrast to the behaviour of complexes **8** and **9**, the treatment of complex [Ru(η⁶-*p*-cymene)Cl{κ²-*P,N*-Ph_2PCH_2P(=NH)Ph_2}][PF_6] **7** with anionic ligands (Br^-, I^-, N_3^-, CN^-, NCO^-) affords, under the same reaction conditions, the cationic derivatives [Ru(η⁶-*p*-cymene)X{κ²-*P,N*-Ph_2PCH_2P(=NH)Ph_2}][PF_6] (X = Br **12a**, I **12b**, N_3 **12c**, CN **12d**, NCO **12e**; 76–92% yield) as the result of the metathesis of the chloride ligand (Scheme 2). This result reflects the lack of lability of the chelating ligand $Ph_2PCH_2P(=NH)Ph_2$ in **7** as it has been also observed in its reaction of synthesis (Scheme 1). Apparently, the presence of bulky and strong electron withdrawing substituents on the iminophosphorane unit induces the lability of the Ru–N bond. Since the analytical and spectroscopic data of **12a**–**e** are comparable to those observed for its precursor **7** they will not be further discussed (see Tables S5 and S6 provided as Supplementary Information †).

(b) Synthesis of [Ru(η⁶-*p*-cymene)Cl(PR_3){κ¹-*P*-Ph_2PCH_2P(=NR)Ph_2}][PF_6] (R = *p*-C_6F_4CN, L = PMe_3 **13a**, PMe_2Ph **13b**, $PMePh_2$ **13c**, PPh_3 **13d**; R = *p*-C_5F_4N, PR_3 = PMe_3 **14a**, PMe_2Ph **14b**, $PMePh_2$ **14c**, PPh_3 **14d**), [Ru(η⁶-*p*-cymene)Cl(py){κ¹-*P*-Ph_2PCH_2P(=NR)Ph_2}][PF_6] (R = *p*-C_6F_4CN **15**; R = *p*-C_5F_4N **16**) and [Ru(η⁶-*p*-cymene)Cl(CNR′){κ¹-*P*-Ph_2PCH_2P(=NR)Ph_2}][PF_6] (R = *p*-C_6F_4CN, R′ = Cy **19a**, 2,6-$C_6H_3Me_2$ **19b**; R = *p*-C_5F_4N, R′ = Cy **20a**, 2,6-$C_6H_3Me_2$ **20b**)

Complexes **8** and **9** react with phosphines (*ca.* 10 equiv.) giving rise to the cationic compounds [Ru(η⁶-*p*-cymene)Cl(PR_3){κ¹-*P*-Ph_2PCH_2P(=NR)Ph_2}][PF_6] (R = *p*-C_6F_4CN, L = PMe_3 **13a**, PMe_2Ph **13b**, $PMePh_2$ **13c**, PPh_3 **13d**; R = *p*-C_5F_4N, PR_3 = PMe_3 **14a**, PMe_2Ph **14b**, $PMePh_2$ **14c**, PPh_3 **14d**) (75–85% yield; Scheme 3) with reaction times dependent on the incoming phosphine (PMe_3, *ca.* 4 h; PMe_2Ph, *ca.* 12 h; $PMePh_2$, *ca.* 24 h; PPh_3, *ca.* 30 h).

Analytical and spectroscopic data (IR and $^{31}P-\{^1H\}$, ^1H, ^{19}F, and $^{13}C-\{^1H\}$) for **13**–**14** strongly support the proposed



	PR_3	R
13a	PMe_3	*p*-C_6F_4CN
13b	PMe_2Ph	*p*-C_6F_4CN
13c	$PMePh_2$	*p*-C_6F_4CN
13d	PPh_3	*p*-C_6F_4CN
14a	PMe_3	*p*-C_5F_4N
14b	PMe_2Ph	*p*-C_5F_4N
14c	$PMePh_2$	*p*-C_5F_4N
14d	PPh_3	*p*-C_5F_4N

Scheme 3 Reactivity of complexes **8**–**9** towards neutral ligands.

formulations (see Tables S7–S10 provided as Supplementary Information †). In particular, the ^{31}P-{^1H} NMR spectra are very informative showing, in addition to the expected resonances of the monodentate phosphine, a doublet signal (^2J(PP) = 35.7–37.2) for the iminophosphorane unit in the range 8.4–13.2 ppm and a doublet of doublets (^2J(PP) = 52.9–57.0 and 35.7–37.2) for the diphenylphosphino group of the Ph_2PCH_2P(=NR)Ph_2 ligands at 19.3–29.3 ppm. In agreement with the chirality of the metal, the methylenic PCH_2P protons become inequivalents appearing in the ^1H NMR spectra as two unresolved multiplets in the range δ_H 1.66–4.66. As expected, the PCH_2P carbon resonates in the ^{13}C-{^1H} NMR spectra as a doublet of doublets (J(CP) = 60.3–80.4 (P(V)) and 13.7–17.5 (P(III))) at δ_C 20.35–24.58. Complexes **8**–**9** also react with pyridine, in dichloromethane at room temperature, to afford the related compounds [Ru(η^6-*p*-cymene)Cl(py){κ^1-*P*-Ph_2PCH_2P(=NR)Ph_2}][PF_6] (R = *p*-C_6F_4CN **15**; R = *p*-C_5F_4N **16**) (Scheme 3) which were isolated in 92 and 84% yield, respectively, and fully characterized (see the Supplementary Information †). In accordance with the lack of hemilabile reactivity of complex **7** towards anionic ligands, no reaction is either observed with phosphines or pyridine.

Although solutions of complexes **8** and **9** in dichloromethane or THF remain unchanged in the presence of isocyanides, the treatment of **8**–**9** with an excess (*ca.* 10 equiv.) of cyclohexyl isocyanide or 2,6-dimethylphenyl isocyanide in acetonitrile slowly (*ca.* 12 h) generates complexes [Ru(η^6-*p*-cymene)Cl(CNR′){κ^1-*P*-Ph_2PCH_2P(=NR)Ph_2}][PF_6] (R = *p*-C_6F_4CN, R′ = Cy **19a**, 2,6-$C_6H_3Me_2$ **19b**; R = *p*-C_5F_4N, R′ = Cy **20a**, 2,6-$C_6H_3Me_2$ **20b**) (73–82% yield; Scheme 4). Elemental analyses and spectroscopic data are in accordance with the proposed formulations (see the Supplementary Information †). The most significant spectroscopic features of **19**–**20** are those concerning the coordinated isocyanide ligand: (i) (IR) the typical absorption band in the range 2138–2181 cm^{-1}, and (ii) (^{13}C-{^1H} NMR) a characteristic doublet signal (^2J(CP) = 9.8–15.8) at *ca.* 146 ppm. The reactions seem to proceed through the acetonitrile complexes [Ru(η^6-*p*-cymene)Cl(N≡CMe){κ^1-*P*-Ph_2PCH_2P(=NR)Ph_2}][PF_6] (R = *p*-C_6F_4CN **17**, R = *p*-C_5F_4N **18**) which are formed when **8** and **9** are dissolved in acetonitrile (Scheme 4) as inferred by ^{31}P-{^1H} NMR spectroscopy which shows signals at 8.7 and 24.6 (d, ^2J(PP) = 37.3) ppm for **17**, and at 10.1 and 25.5 (d, ^2J(PP) = 35.7) ppm for **18**. All attempts to isolate **17** and **18** failed, leading instead to the precursors **8** and **9** quantitatively after evaporation of the solvent. The reversibility of this process evidences clearly the hemilability of these heterodifunctional P/N-donor ligands. On the basis of these observations, the formation of isocyanide complexes **19**–**20** in acetonitrile can be explained assuming that complexes **17**–**18** are initially generated and subsequently undergo the displacement of the labile acetonitrile ligand by the corresponding isocyanide.

Synthesis of ruthenium(IV) complexes [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2-{κ^1-*P*-Ph_2PCH_2P(=NR)Ph_2}] (R = $SiMe_3$ **21**, *p*-C_6F_4CN **22**, *p*-C_5F_4N **23**) and [Ru(η^3:η^3-$C_{10}H_{16}$)Cl{κ^2-*P,N*-Ph_2PCH_2P(=NH)Ph_2}][BF_4] **24**

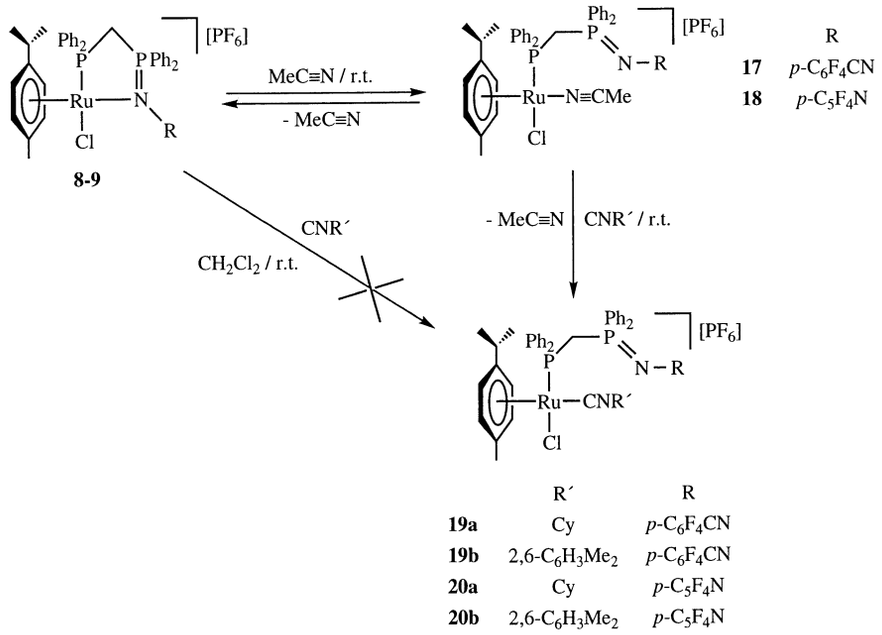
The coordination chemisty of the dimeric Ru(IV) complex [{Ru(η^3:η^3-$C_{10}H_{16}$)(μ-Cl)Cl}$_2$] is clearly related to that of [{Ru(η^6-arene)(μ-Cl)Cl}$_2$] although the former has been much less developed.[23] In this context, we believed it to be of interest to compare the hemilabile properties of the iminophosphorane-phosphine ligands **1**–**3** in both metallic fragments. As expected, the treatment of dichloromethane solutions of [{Ru(η^3:η^3-$C_{10}H_{16}$)(μ-Cl)Cl}$_2$] with two equivalents of **1**–**3** results in the cleavage of the chloride bridges and the clean formation of mononuclear bis(allyl)-ruthenium(IV) complexes [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2-{κ^1-*P*-Ph_2PCH_2P(=NR)Ph_2}] (R = $SiMe_3$ **21**, *p*-C_6F_4CN **22**, *p*-C_5F_4N **23**; 77–97% yield) (Scheme 5).

Elemental analyses and NMR spectroscopic data of compounds **21**–**23** support the proposed formulations (details are given in the Supplementary Information †). Significantly, the ^{31}P-{^1H} NMR spectra display doublet signals (^2J(PP) = 32.9–35.4) in the ranges δ_P −7.6 to 7.5 (Ph_2P=N) and 17.9–19.5 (Ph_2P) which compare well with those of the complexes [Ru(η^6-*p*-cymene)Cl_2-{κ^1-*P*-Ph_2PCH_2P(=NR)Ph_2}] (R = $SiMe_3$ **4**, *p*-C_6F_4CN **5**, *p*-C_5F_4N **6**). In addition, both ^1H and ^{13}C-{^1H} NMR spectra show a single set of signals for the two allylic moieties suggesting that the two halves of the 2,7-dimethylocta-2,6-diene-1,8-diyl skeleton are in equivalent environments, as expected for the formation of a simple equatorial adduct.[23]

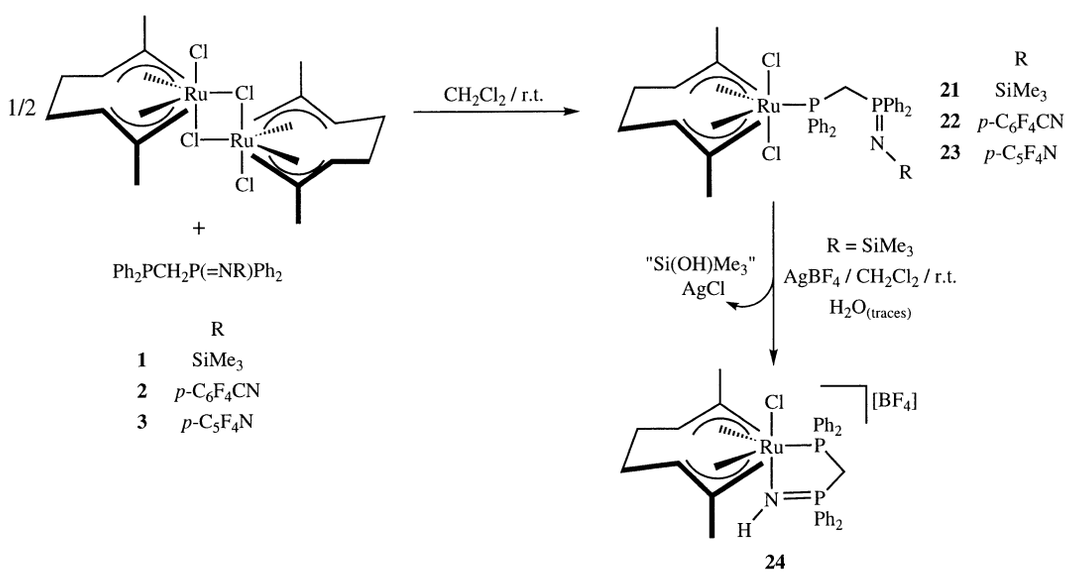
However, all attempts to generate cationic complexes structurally related to **8**–**9**, by treatment of fluorinated derivatives **22**–**23** with $NaPF_6$ or $AgBF_4$ under different reaction conditions failed, and instead complicated reaction mixtures of uncharacterized products were obtained. Remarkably, the ^1H NMR spectra of these mixtures do not show the presence of the octadienediyl moiety. This seems to indicate, by comparison with previous observations,[24] that a reductive elimination of the organic fragment to give ruthenium(II) species has taken place. In contrast, we have found that [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2-{κ^1-*P*-Ph_2PCH_2P(=NSiMe_3)Ph_2}] **21** cleanly reacts with $AgBF_4$, in dichloromethane at room temperature, to afford the cationic derivative [Ru(η^3:η^3-$C_{10}H_{16}$)Cl{κ^2-*P,N*-Ph_2PCH_2P(=NH)Ph_2}]-[BF_4] **24** (96% yield; Scheme 5) after cleavage of the N-$SiMe_3$ bond. This different behaviour can be explained on the basis of the steric hindrance between the bulky octadienediyl moiety and the iminophosphorane substituent. This effect seems to decrease when the fluoro-aromatic rings of **22**–**23** are replaced by hydrogen, allowing the chelation of the ligand. The reactivity of **24** towards neutral and anionic ligands has been also explored but complicated reaction mixtures of uncharacterized species were in all the cases observed.

Conclusions

In this work the preparation of the first ruthenium(II) and (IV) complexes containing iminophosphorane-phosphines Ph_2PCH_2P(=NR)Ph_2 starting from the readily accessible dimers [{Ru(η^6-*p*-cymene)(μ-Cl)Cl}$_2$] and [{Ru(η^3:η^3-$C_{10}H_{16}$)(μ-Cl)Cl}$_2$] is reported. They belong to two types of derivatives: (a) κ^1-*P*-monodentate complexes [Ru(η^6-*p*-cymene)Cl_2-{κ^1-*P*-Ph_2PCH_2P(=NR)Ph_2}] (R = $SiMe_3$, *p*-C_6F_4CN, *p*-C_5F_4N) and [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2-{κ^1-*P*-Ph_2PCH_2P(=NR)Ph_2}] (R = $SiMe_3$, *p*-C_6F_4CN, *p*-C_5F_4N), and (b) κ^2-*P,N*-cationic complexes [Ru(η^6-*p*-cymene)Cl{κ^2-*P,N*-Ph_2PCH_2P(=NR)Ph_2}][PF_6] (R =



Scheme 4 Reactivity of complexes **8**–**9** towards isocyanides.



Scheme 5 Coordination of iminophosphorane-phosphine ligands on a bis(allyl)-ruthenium(IV) moiety.

H, *p*-C_6F_4CN, *p*-C_5F_4N) and [Ru(η^3:η^3-$C_{10}H_{16}$)Cl{κ^2-*P,N*-$Ph_2PCH_2P(=NH)Ph_2$}][BF_4]. For the first time it has been shown that iminophosphorane-phosphines can act as hemilabile ligands providing the presence of bulky and strong electron withdrawing substituents (R = *p*-C_6F_4CN, *p*-C_5F_4N). Thus, we have found that the Ru-N bond in chelate complexes [Ru(η^6-*p*-cymene)Cl{κ^2-*P,N*-$Ph_2PCH_2P(=NR)Ph_2$}][PF_6] (R = *p*-C_6F_4CN, *p*-C_5F_4N) can be readily cleaved, under very mild reaction conditions, by a large variety of anionic and neutral ligands. The chelate ring opening processes have led to the formation of the stable complexes [Ru(η^6-*p*-cymene)X_2{κ^1-*P*-$Ph_2PCH_2P(=NR)Ph_2$}] (X = Br, I, N_3, CN, NCO) and [Ru(η^6-*p*-cymene)Cl(L){κ^1-*P*-$Ph_2PCH_2P(=NR)Ph_2$}][PF_6] (L = PR_3, py, CNR′), respectively. Moreover, complexes [Ru(η^6-*p*-cymene)Cl{κ^2-*P,N*-$Ph_2PCH_2P(=NR)Ph_2$}][PF_6] (R = *p*-C_6F_4CN, *p*-C_5F_4N) undergo a reversible chelate ring opening process in acetonitrile (Scheme 4). In conclusion, the synthesis of these series of ruthenium complexes has shown that these heterodifunctional P/N-donor ligands can be used as good hemilabile ligands. Studies devoted to its application in homogeneous catalysis are now in progress.

Experimental

General comments

The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. All reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by standard methods and distilled under nitrogen before use. The compounds [{Ru(η^6-*p*-cymene)(μ-Cl)Cl}$_2$],[16] [{Ru(η^3:η^3-$C_{10}H_{16}$)-(μ-Cl)Cl}$_2$][23b] and $Ph_2PCH_2P(=NR)Ph_2$ (R = $SiMe_3$, *p*-C_6F_4CN, *p*-C_5F_4N)[6b,10a] were prepared by following the methods reported in the literature. Analytical and spectroscopic data for all he complexes reported in this paper have been provided as Supplementary Information.†

Preparations

[Ru(η^6-*p*-cymene)Cl_2{κ^1-*P*-$Ph_2PCH_2P(=NR)Ph_2$}] (R = $SiMe_3$ 4, *p*-C_6F_4CN 5, *p*-C_5F_4N 6). *General procedure.* A solution of [{Ru(η^6-*p*-cymene)(μ-Cl)Cl}$_2$] (0.245 g, 0.4 mmol) and the

corresponding iminophosphorane-phosphine **1**–**3** (0.8 mmol) in 30 cm^3 of dichloromethane was stirred at room temperature for 1 h and then evaporated to dryness. The orange solid residue was washed with pentane (3 × 10 cm^3) and dried *in vacuo*. **4**: Yield: 0.473 g, 76%. **5**: Yield: 0.548 g, 78%. **6**: Yield: 0.472 g, 69%.

[Ru(η⁶-*p*-cymene)Cl{κ²-*P,N*-$Ph_2PCH_2P(=NR)Ph_2$}][PF_6] (R = H 7, *p*-C_6F_4CN 8, *p*-C_5F_4N 9). *Method A.* A solution of the corresponding neutral complex [Ru(η⁶-*p*-cymene)Cl_2{κ¹-*P*-$Ph_2PCH_2P(=NR)Ph_2$}] **4**–**6** (0.5 mmol) and $NaPF_6$ (0.084 g, 0.5 mmol for **4**; 1g, 6 mmol for **5**–**6**) in 40 cm^3 of methanol was stirred at room temperature for 12 h and then evaporated to dryness. The residue was extracted with *ca.* 20 cm^3 of dichloromethane, the suspension filtered through Kieselguhr, and the resulting solution concentrated to dryness. The orange solid obtained was washed with diethyl ether (3 × 20 cm^3) and dried *in vacuo*. **7**: Yield: 0.322 g, 79%. **8**: Yield: 0.415 g, 84%. **9**: Yield: 0.385 g, 80%.

Method B. A suspension of [{Ru(η⁶-*p*-cymene)(μ-Cl)Cl}$_2$] (0.153 g, 0.25 mmol), the corresponding iminophosphorane-phosphine **1**–**3** (0.5 mmol) and $NaPF_6$ (0.084 g, 0.5 mmol for **4**; 1 g, 6 mmol for **5**–**6**) in 40 cm^3 of methanol was stirred at room temperature for 12 h and then evaporated to dryness. The residue was extracted with *ca.* 20 cm^3 of dichloromethane, the suspension filtered through Kieselguhr, and the resulting solution concentrated to dryness. The orange solid obtained was washed with diethyl ether (3 × 20 cm^3) and dried *in vacuo*. Yields ≈ 75%.

[Ru(η⁶-*p*-cymene)X_2{κ¹-*P*-$Ph_2PCH_2P(=NR)Ph_2$}] (R = *p*-C_6F_4CN, X = Br 10a, I 10b, N_3 10c, CN 10d, NCO 10e; R = *p*-C_5F_4N, X = Br 11a, I 11b, N_3 11c, CN 11d, NCO 11e). *General procedure*. A solution of the corresponding complex [Ru(η⁶-*p*-cymene)Cl{κ²-*P,N*-$Ph_2PCH_2P(=NR)Ph_2$}][PF_6] **8**–**9** (0.5 mmol) and the appropriate sodium salt NaX (8 mmol) in 40 cm^3 of methanol was stirred at room temperature for 8 h and then evaporated to dryness. The residue was extracted with *ca.* 90 cm^3 of diethyl ether, the suspension filtered through Kieselguhr, and the resulting solution concentrated to dryness to give a yellow–orange solid. **10a**: Yield: 0.401 g, 83%. **10b**: Yield: 0.414 g, 78%. **10c**: Yield: 0.352 g, 79%. **10d**: Yield: 0.296 g, 69%. **10e**: Yield: 0.316 g, 71%. **11a**: Yield: 0.415 g, 88%. **11b**: Yield: 0.389 g, 75%. **11c**: Yield: 0.377 g, 87%. **11d**: Yield: 0.384 g, 92%. **11e**: Yield: 0.317 g, 73%.

[Ru(η⁶-*p*-cymene)X{κ²-*P,N*-$Ph_2PCH_2P(=NH)Ph_2$}][PF_6] (X = Br 12a, I 12b, N_3 12c, CN 12d, NCO 12e). *General procedure*. A solution of [Ru(η⁶-*p*-cymene)Cl{κ²-*P,N*-$Ph_2PCH_2P(=NH)Ph_2$}][PF_6] **7** (0.407 g, 0.5 mmol) and the corresponding sodium salt NaX (8 mmol) in 40 cm^3 of methanol was stirred at room temperature for 6 h and then evaporated to dryness. The residue was extracted with *ca.* 20 cm^3 of dichloromethane, the suspension filtered through Kieselguhr, and the resulting solution concentrated to dryness. The yellow–orange solid obtained was washed with diethyl ether (3 × 20 cm^3) and dried *in vacuo*. **12a**: Yield: 0.378 g, 88%. **12b**: Yield: 0.344 g, 76%. **12c**: Yield: 0.377 g, 92%. **12d**: Yield: 0.358 g, 89%. **12e**: Yield: 0.345 g, 84%.

[Ru(η⁶-*p*-cymene)Cl(PR_3){κ¹-*P*-$Ph_2PCH_2P(=NR)Ph_2$}][PF_6] (R = *p*-C_6F_4CN, PR_3 = PMe_3 13a, PMe_2Ph 13b, $PMePh_2$ 13c, PPh_3 13d; R = *p*-C_5F_4N, PR_3 = PMe_3 14a, PMe_2Ph 14b, $PMePh_2$ 14c, PPh_3 14d). *General procedure*. A solution of the corresponding complex [Ru(η⁶-*p*-cymene)Cl{κ²-*P,N*-$Ph_2PCH_2P(=NR)Ph_2$}][PF_6] **8**–**9** (0.5 mmol) and the appropriate phosphine (5 mmol) in 40 cm^3 of dichloromethane was stirred at room temperature for the time indicated below and then evaporated to dryness. The yellow solid residue was washed with diethyl ether (3 × 30 cm^3) and dried *in vacuo*. **13a**: Time: 4 h. Yield: 0.452 g, 85%. **13b**: Time: 12 h. Yield: 0.473 g, 84%. **13c**: Time: 24 h. Yield: 0.463 g, 78%. **13d**: Time: 30 h. Yield: 0.500 g, 80%. **14a**: Time: 4 h. Yield: 0.395 g, 76%. **14b**: Time: 12 h. Yield: 0.435 g, 79%. **14c**: Time: 24 h. Yield: 0.437 g, 75%. **14d**: Time: 30 h. Yield: 0.472 g, 77%.

[Ru(η⁶-*p*-cymene)Cl(py){κ¹-*P*-$Ph_2PCH_2P(=NR)Ph_2$}][PF_6] (R = *p*-C_6F_4CN 15; R = *p*-C_5F_4N 16). *General procedure*. A solution of the corresponding complex [Ru(η⁶-*p*-cymene)Cl{κ²-*P,N*-$Ph_2PCH_2P(=NR)Ph_2$}][PF_6] **8**–**9** (0.5 mmol) and pyridine (0.404 cm^3, 5 mmol) in 40 cm^3 of dichloromethane was stirred at room temperature for 12 h and then evaporated to dryness. The yellow solid residue was washed with diethyl ether (3 × 30 cm^3) and dried *in vacuo*. **15**: Yield: 0.491 g, 92%. **16**: Yield: 0.438 g, 84%.

[Ru(η⁶-*p*-cymene)Cl(CNR′){κ¹-*P*-$Ph_2PCH_2P(=NR)Ph_2$}][PF_6] (R = *p*-C_6F_4CN, R′ = Cy 19a, 2,6-$C_6H_3Me_2$ 19b; R = *p*-C_5F_4N, R′ = Cy 20a, 2,6-$C_6H_3Me_2$ 20b). *General procedure*. A solution of the corresponding complex [Ru(η⁶-*p*-cymene)Cl{κ²-*P,N*-$Ph_2PCH_2P(=NR)Ph_2$}][PF_6] **8**–**9** (0.5 mmol) and the appropriate isocyanide (5 mmol) in 40 cm^3 of acetonitrile was stirred at room temperature for 12 h and then evaporated to dryness. The yellow solid residue was washed with diethyl ether (3 × 30 cm^3) and dried *in vacuo*. **19a**: Yield: 0.422 g, 77%. **19b**: Yield: 0.425 g, 76%. **20a**: Yield: 0.440 g, 82%. **20b**: Yield: 0.400 g, 73%.

[Ru(η³:η³-$C_{10}H_{16}$)Cl_2{κ¹-*P*-$Ph_2PCH_2P(=NR)Ph_2$}] (R = $SiMe_3$ 21, *p*-C_6F_4CN 22, *p*-C_5F_4N 23). *General procedure* A solution of [{Ru(η³:η³-$C_{10}H_{16}$)(μ-Cl)Cl}$_2$] (0.616 g, 1 mmol) and the corresponding iminophosphorane-phosphine **1**–**3** (2 mmol) in 30 cm^3 of dichloromethane was stirred at room temperature for 5 min and then evaporated to dryness. The yellow solid residue was washed with hexane (3 × 10 cm^3) and dried *in vacuo*. **21**: Yield: 1.482 g, 95%. **22**: Yield: 1.708 g, 97%. **23**: Yield: 1.319 g, 77%.

[Ru(η³:η³-$C_{10}H_{16}$)Cl{κ²-*P,N*-$Ph_2PCH_2P(=NH)Ph_2$}][BF_4] 24. A solution of [Ru(η³:η³-$C_{10}H_{16}$)C_{l2}{κ¹-*P*-$Ph_2PCH_2P(=NSiMe_3)Ph_2$}] **21** (0.3 g, 0.386 mmol) in 20 cm^3 of dichloromethane was treated, at room temperature and in the dark, with $AgBF_4$ (0.08 g, 0.41 mmol) for 1 h. The resulting suspension was then filtered through Kieselguhr and the filtrate evaporated to dryness. The yellow solid residue was washed with diethyl ether (3 × 20 cm^3) and dried *in vacuo*. Yield: 0.218 g, 96%.

X-Ray crystal structure determination of [Ru(η⁶-*p*-cymene)-(κ¹-*N*-NCO)$_2${κ¹-*P*-$Ph_2PCH_2P(=N$-*p*-$C_6F_4CN)Ph_2$}]·CH_2Cl_2 10e

Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a saturated solution of the complex in dichlorometane. Data collection, crystal, and refinement parameters are collected in Table 1. Diffraction data were recorded on a Nonius Kappa CCD single crystal diffractometer using Cu-Kα radiation. Crystal-detector distance was fixed at 29 mm and a total of 1243 frames were collected using the oscillation method, with 2° oscillation and 40 s exposure time per frame. Data collection strategy was calculated with the program Collect.[25] Data reduction and cell refinement were performed with the programs HKL Denzo and Scalepack.[26] Unit cell dimensions were determined from 7669 reflections with θ between 2 and 71°. Symmetry equivalents and multiple observations were averaged, R_{merge} = 0.079, resulting in 8148 unique reflections of which 6753 were observed with $I > 2\sigma(I)$. Final mosaicity was 0.444(3)°. All data completeness was 99.0%.

The structure was solved by Patterson methods using the program DIRDIF.[27] Isotropic full-matrix least-squares refinement on F^2 using SHELXL-97 was performed.[28] During the final stages of the refinement, all positional parameters and the anisotropic thermal parameters of all the non-H atoms were refined. A highly disordered CH_2Cl_2 solvent molecule was found which was isotropically refined. The H-atoms were geometrically placed and their coordinates were refined riding on

Table 1 Crystal data and structure refinement for **10e**

Empirical formula	$RuC_{44}H_{36}F_4N_4O_2P_2 \cdot CH_2Cl_2$
Formula weight	976.70
T/K	200(2)
λ/Å	1.54184
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a/Å	12.5484(4)
b/Å	12.7604(5)
c/Å	13.8396(7)
α/°	101.654(3)
β/°	92.512(3)
γ/°	91.765(3)
V/Å^3	2166.49(15)
Z	2
D_c/g cm^{-3}	1.497
μ/mm^{-1}	5.271
F(000)	992
Crystal size/mm	0.28 × 0.22 × 0.08
Theta range for data collection/°	3.26–70.01
Index ranges	$-15 \le h \le 15$, $-15 \le k \le 15$, $0 \le l \le 16$
Reflections collected/unique	8149/8148 [R(int) = 0.0000]
Completeness to theta = 70.01°	99.0%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8148/0/541
Goodness-of-fit on F^2	1.098
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0637$, $wR_2 = 0.1836$
R indices (all data)	$R_1 = 0.0708$, $wR_2 = 0.1975$
Largest diff. peak and hole/e Å^{-3}	2.872 and −1.357

their parent atoms. The final cycle of full-matrix least-squares refinement based on 8148 reflections and 541 parameters converged to final values of R_1 ($F^2 > 2\sigma(F^2)$) = 0.0637, wR_2 ($F^2 > 2\sigma(F^2)$) = 0.1836, R_1 (F^2) = 0.0708, $wR_2(F^2)$ = 0.1975. The function minimized was $[\Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o^2)]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (0.1077P)^2]$ with $\sigma(F_o^2)$ from counting statistics and P = (Max (F_o^2, 0) + $2F_c^2$)/3. The maximum residual electron density is located near to the disordered solvent molecule. Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[29] Geometrical calculations were made with PARST.[30] The crystallographic plots were made with PLATON.[31] All calculations were performed at the Scientific Computer Centre of the University of Oviedo using VAX and DEC-ALPHA computers.

CCDC reference number 174365.

See http://www.rsc.org/suppdata/dt/b1/b110442j/ for crystallographic data in CIF or other electronic format.

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