Organoruthenium Complexes Containing Hemilabile Phosphinodicarboxamide Ligands

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Supporting information (full experimental details, characterization, crystallographic data and CIF files) can be found at XXXXXXXXXXX.

Abstract

Ruthenium complexes of hemilabile phosphinocarboxamide ligands, and their use to form metallacycles using halide abstraction/deprotonation reactions are reported. Thus, [Ru(*p*-cym){$PPh_2C(=O)NHR$}Cl_2; R = ^{i}Pr (**1**), Ph (**2**), *p*-tol (**3**)] and [Ru(*p*-cym){$PPh_2C(=O)N(R)C(=O)N(H)R$}Cl_2; R = Ph (**4**), *p*-tol (**5**)] were synthesized from $[(p\text{-cym})RuCl_2]_2$ (*p*-cym = *para*-cymene) and phosphinocarboxamides or phosphinodicarboxamides, respectively. Single crystal X-ray diffraction measurements on **1**–**5** reveal coordination to ruthenium through the phosphorus donor, with an intramolecular hydrogen bond between the amine-bound proton and a metal-bound chloride. Six-membered metallacycles formed by halide abstraction/deprotonation of complexes **4** and **5** afforded [Ru(*p*-cym){κ^2-*P,N*-$PPh_2C(=O)N(R)C(=O)NR$}Cl] [R = Ph (**6**), *p*-tol (**7**)]. These species exist as a mixture of two rotational isomers in solution, as demonstrated by NMR spectroscopy.

Introduction

Hemilabile ligands incorporating both hard and soft donor atoms continue to attract attention[1] and have found applications in coordination chemistry,[1–3] biomedicine,[4,5] enantioselective catalysis[6,7] and supramolecular and self-assembled arrays.[8] Recently, we reported the syntheses of functionalized phosphinocarboxamides (PCAs) and a new family of phosphinodicarboxamides (PDCAs) through the catalytic hydrophosphination of isocyanates.[9] These compounds possess hard (N or O) and soft (P) donor atoms that allows for hemilabile coordination, thereby enabling their binding to a wide range of metal centres in diverse coordination modes.[10] Despite this, PCAs have found limited use as ligands[1–3,11] and PDCAs have not been investigated in metal complexation reactions. Relevant co-ordination chemistry includes: (i) the diinsertion of phenyl isocyanates into an amine bond using lanthanide metal centres to form $Cp_2Ln[\eta^2{:}\eta^1$-PyNCON(Ph)CONHPh] (Ln = Yb, Er, Y, Dy, Gd; Py = 2-pyridyl), from which substituted ureas can be prepared;[12] (ii) the use of primary phosphinocarboxamides in the syntheses of *cis*-$[Mo(CO)_4(PH_2C(=O)NH_2)_2]$[11] and [Ru(*p*-cym){$PH_2C(=O)N(HCy)Cl_2$}] (Cy = cyclohexyl)[2] and (iii) the reaction of $Fe(\eta^5\text{-}C_5H_4N(H)C(=O)PPh_2)_2$ with $PtX_2(PPh_3)_2$ (X = Cl, Br) that has allowed for the first selective synthesis of M_4L_6 cage complexes, facilitated by hydrogen bonding interactions between the PCA moiety and the halide ion.[13]

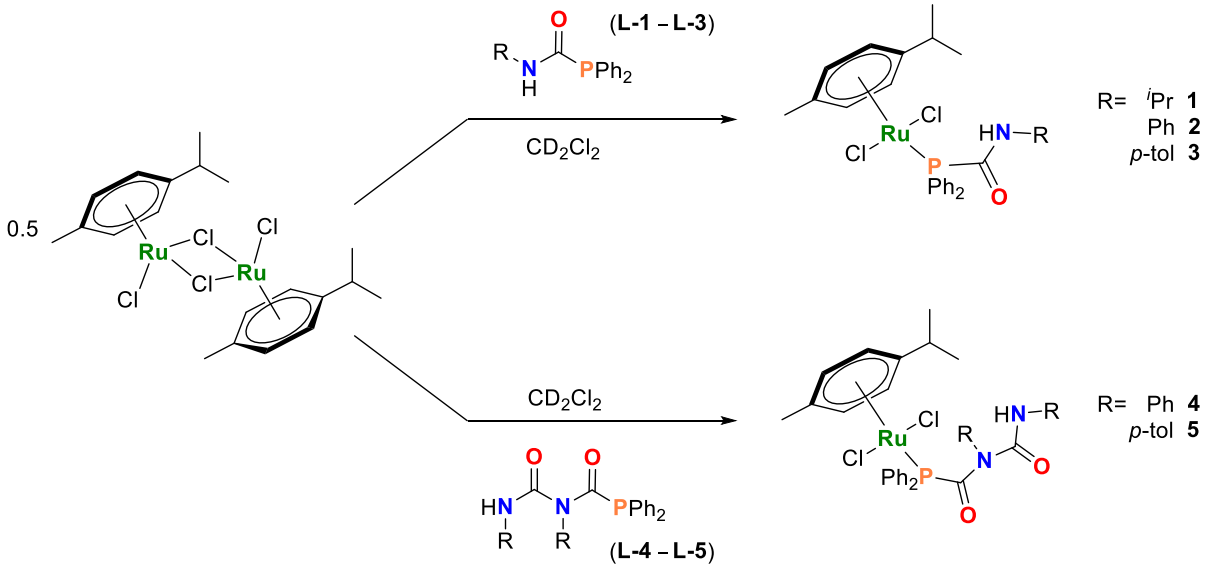
Half-sandwich ruthenium complexes have been widely studied as potential catalysts,[14–23] due to their ease of interconversion to other Ru(0) and Ru(II) complexes.[17] In particular, [(η^6-arene)$RuCl_2(PR_3)$] (R = aryl or alkyl)[10] complexes are effective precursors for a variety of catalytic and stoichiometric organic transformations.[18,24] Notable examples include the transfer hydrogenation of ketones and benzaldehydes by [Ru(*p*-cym){OC_6H_4-2-$CH_2NHC_6H_4$-*p*-Me}Cl],[15,16,25] the isomerization of olefins such as allylbenzene and 1-octene by [Ru(*p*-cym)*L*Cl] {*L* = 4-(phenylazo)resorcinol},[14] and a wide range of heteroatom insertion reactions involving cationic allenylidene and cumulenylidene complexes such as [Ru=(C=C=CPh_2)(η^5-1,2,3-$Me_3C_9H_4$)(CO)PPh_3)]$^+$.[21] Thus, the *p*-cymene-ruthenium(II) fragment is an ideal choice for probing the coordination chemistry of new PDCAs, and for comparisons with the analogous PCA-containing complexes.

Herein, we describe the syntheses of [Ru(*p*-cym){PPh_2C(=O)NHR}Cl_2; R = ^{i}Pr (**1**), Ph (**2**), *p*-tol (**3**)] and [Ru(*p*-cym){PPh_2C(=O)N(R)C(=O)N(*H*)R}Cl_2; R = Ph (**4**), *p*-tol (**5**)]. This study includes the first reported examples of PDCAs as monodentate and bidentate ligands, with the latter coordination mode resulting in six-membered metallacycles.

Results and Discussion

Synthesis and Characterization of [Ru(*p*-cym){PPh_2C(=O)N(H)R}Cl_2] [R = ^{i}Pr (1) , Ph (2), *p*-tol (3)] and [Ru(*p*-cym){PPh_2C(=O)N(R)C(=O)N(*H*)R}Cl_2] ([R = Ph (4), *p*-tol (5)]

A solution of [Ru(*p*-cym)$Cl_2]_2$ and **L-1** (PPh_2C(=O)N(H)^{i}Pr) in a 1:2 ratio in dichloromethane was stirred at room temperature overnight, which, after removal of solvent and extraction into toluene afforded **1** as a dark red solid (Scheme 1). The use of phosphinocarboxamides with nitrogen-substituted aromatic groups (**L-2** and **L-3**) affords the analogous compounds [Ru(*p*-cym){Ph_2PC(=O)N(*H*)R}Cl_2; R= Ph (**2**) and *p*-tol (**3**)] (Scheme 1). Pure samples of **1**–**3** were isolated in moderate to excellent yields (**1**, 39%; **2**, 53%; **3**, 99%). These compounds exist as air-stable bright-red crystalline solids and have been characterized by NMR and IR spectroscopies, mass spectrometry, single crystal X-ray diffraction and elemental analyses (see SI for full details).



Scheme 1. Synthesis and structure of **1**–**5**. Reaction conditions: 0.5 eq. [Ru(*p*-cym)$Cl_2]_2$ and 1 eq. **L-1**–**L-5** at room temperature, 10 minutes.

Table 1. Selected NMR spectroscopic data δ (ppm) for the free PCA/PDCAs **L-1**–**L-5**, and complexes **1**-**7**.

Compound	^{31}P Free PCA/PDCA ligand[a]	^{31}P PCA/PDCA complex[b]	$^{13}C\{^{1}H\}_{C=O}$ PCA/PDCA complex[b]	$^{1}H_{NH}$ PCA/PDCA complex[b]
1	-4.0	29.8[a]	167.4[a)]	8.6[a]
2	-0.2	37.2	167.6	10.1
3	-0.9	36.6	167.5	10.0
4	8.3	33.5	178.2 / 177.7[c]	9.2
5	8.0	33.8	177.9 /177.5[c]	9.2
6	-	52.6	-[d]	-
7	-	52.3	170.9 / 162.1[c]	-

[a] Chemical shifts reported in ppm in C_6D_6. [b] Chemical shifts reported in ppm in CD_2Cl_2. [c] Chemical shifts for $Ph_2P_{(C=O)}$ and $N_{(C=O)}$ in ppm. [d] Signal not observed.

In parallel, the phosphinodicarboxamides $PPh_2C(=O)NPhC(=O)NHR$ (R = Ph **L-4**, *p*-tol **L-5**)[9] were reacted with $[Ru(p\text{-cym})Cl_2]_2$ (Scheme 1) under similar conditions, affording $[Ru(p\text{-cym})\{PPh_2C(=O)N(R)C(=O)N(H)R\}Cl_2]$; {R= Ph (**4**) and *p*-tol (**5**)}. Unlike **1**–**3**, complexes **4** and **5** are sparingly soluble in low-polarity hydrocarbons such as benzene and toluene. Characterization using NMR spectroscopy in CD_2Cl_2 indicate only one species in solution for compounds **1**-**5** (Tables 1 and **S1** and Figures **S6**-**S15**). These compounds possess bilateral symmetry in the *p*-cymene ligand as shown by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopic determinations in solution. Thus, in the $^{13}C\{^{1}H\}$ NMR spectra of **1**–**5**, the non-quaternary carbons of the *p*-cymene appear as doublets due to scalar coupling with the phosphorus atom of the PCA/PDCA ligand ($^{2}J_{CP}$ = 4 and 6 Hz; see Figure **S8**).[26] While the carbonylic PCA/PDCAs fragments are upfield shifted with respect to their corresponding free ligand (**L1**–**L5**) (Table 1) [*e.g.* $\delta_{C=O}$ = 167 (***1***) *vs.* 175 (**L-1**) ppm], with a downfield shift observed in the ^{31}P NMR, upon complexation [*e.g.* δ_P = 29.8 (**1**) *vs.* -4.0 (**L-1**) ppm] (Figures **S6**-**S15**).[9,11,27–29] Similar deshielding for the amide N*H* signals, is also observed in the ^{1}H NMR spectra of compounds **1**-**3** [*e.g.* δ_H = 8.63 (**1**) *vs.* 5.35 (**L-1**) ppm]. This is most likely a consequence of intramolecular hydrogen bonding interactions upon introduction of the $[Ru(p\text{-cym})Cl_2]$ moiety (*vide infra*).

Crystals of compounds **1**–**5** suitable for single crystal X-ray diffraction investigations were obtained from toluene solutions at room temperature (Figure 1 and Figures **S1**–**S5**). In the solid-state, **1**–**5** feature a pseudo-octahedral geometry in a classical piano-stool arrangement, in which the coordination sphere consists of an η^6-bound *p*-cymene, two chloride ligands, and the P donor from the PCA/PDCA ligand (Figure 1). In the particular case of the structures of **4** and **5**, the core of the PDCA ligands is twisted compared to the free ligand,[9] which most likely arises from $\pi\cdots\pi$ stacking interactions

between an aminic aryl group and the phenyl phosphine fragment, and highlights the conformational flexibility of the PDCA ligand [$C17_{plane}$–$C24_{plane}$ = 3.635(3) Å (**4**); $C23_{plane}$–$C9_{plane}$ = 3.540(2) Å (**5**)]. The Ru–Cl and Ru–P distances for **1**–**5** (Table 2), are similar to related phosphorus-bound ruthenium compounds,[2,15,16,24,25,30] such as [Ru(*p*-cym){PH_2(CO)N*H*Cy}Cl_2] and [Ru(*p*-cym){PPh_2C≡CPh}Cl_2] (Ru–Cl; ≈ 2.40 Å , Ru–P; ≈ 2.35 Å).[2,24] In addition, complexes **1**-**5** present intramolecular hydrogen bonding between the amidic proton and one of the metal-bound chlorides in the solid-state. Particularly, and due to the interaction between H1 and Cl1, the distances Ru1-Cl1 and Ru1-Cl2 are not equivalent; this is most noticeable in the determinations for **4** and **5** (Table 2).

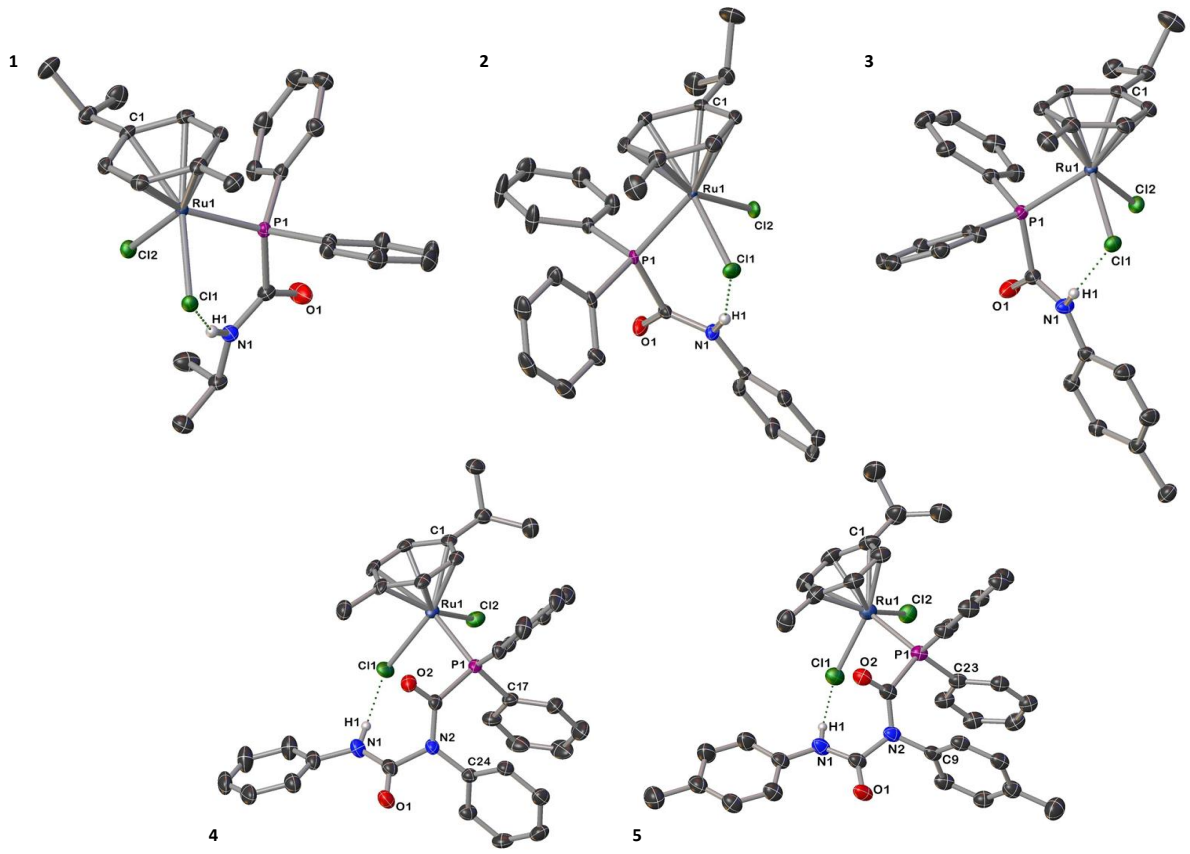


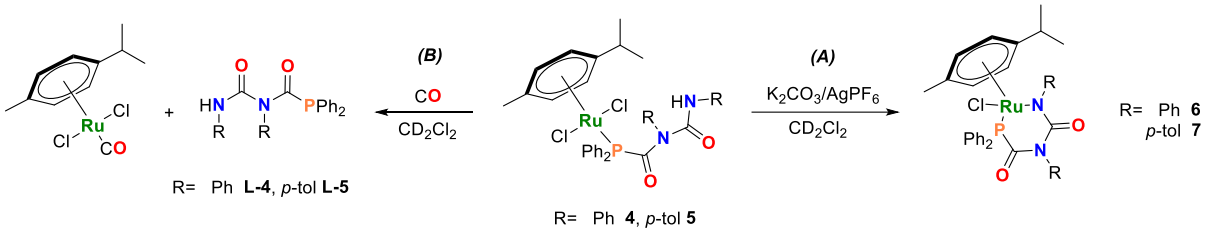
Figure 1. Molecular structures of PCA-coordinated compounds **1**–**3** (*above*) and PDCA-bound complexes **4**-**5** (*below*), with anisotropic displacement ellipsoids set at 50% probability. Solvent of crystallization and carbon-bound hydrogen atoms are omitted for clarity.

Table 2: Selected bond lengths (Å) and angles (°) for **1**–**5**.

	1	**2**	**3**	**4**	**5**
$C1_{plane}$–Ru1	1.7010(8)	1.7007(10)	1.6989(7)	1.7007(9)	1.702(2)
Ru1–Cl1	2.4183(5)	2.4142(6)	2.4171(4)	2.4295(5)	2.4302(11)
Ru1–Cl2	2.4115(5)	2.4151(6)	2.4078(4)	2.3943(6)	2.3974(10)
Ru1–P1	2.3476(5)	2.3448(6)	2.3517(4)	2.3677(6)	2.3635(10)
H1···Cl1	2.53(2)	2.3455(6)	2.28(2)	2.3703(3)	2.44(5)
Cl1–Ru1–P1	86.96(2)	85.17(2)	90.44(2)	87.46(2)	86.49(4)
Cl2–Ru1–P1	87.35(2)	86.87(2)	83.29(2)	89.34(2)	89.70(4)

Synthesis and Characterization of [Ru(*p*-cym){κ^2-*P,N*-$PPh_2C(=O)N(R)C(=O)NR$}Cl] ([R = Ph (6), *p*-tol (7)].

With the intention to synthesize six-membered metallacycles *via* intramolecular cyclization, compounds **4** and **5** were reacted with K_2CO_3 and $AgPF_6$ in CD_2Cl_2 at room temperature [Scheme 2 (***A***)], affording **6** and **7**, respectively (Figures **S16**-**S22**). In contrast, compound **2** showed no reaction under the same conditions. It is likely that the formation of the four-membered metallacycle is prohibited due to the higher ring strain resulting from the shorter PCA backbone.



Scheme 2. (***A***) Formation of six-membered metallacycles (**6** and **7**). Reaction conditions: 1 eq. **4** or **5**, 3 eq. K_2CO_3 and 1.3 eq. $AgPF_6$, room temperature. (***B***) Ligand replacement reaction upon exposure to CO. Reaction conditions: 1 eq. of **4** or **5**, excess CO, room temperature.

The ^{31}P NMR spectroscopic resonances for the cyclized products **6** and **7** are shifted downfield with respect to the corresponding monodenate complexes **4** and **5** (Table 1). This is in line with previously reported six-membered *N,P*-metallacycles, such as [Ru-κ^3-*NNP*-{HCl(CO)}]; [NNP = 3-(di-*tert*-butylphosphino)-*N*-[(1-methyl-1*H*-imidazol-2-yl)methyl]propylamine] (Figures **S19** and **S24**).[27–29] Our NMR spectroscopic studies support the structure proposed in Scheme 2 (Figures **S17**–**S18**, **S21**–**S23**, **S26**–**S28**); and we propose that upon initial coordination (**6**–**7**), reaction with K_2CO_3 can deprotonate the PDCA amide. However, it is not until one of the two coordinate halides is removed by $AgPF_6$, that formal cyclization takes place. This assertion has been corroborated by deprotonation experiments, in absence of $AgPF_6$. Further halide replacement by $[PF_6]^-$ has been ruled out by means of NMR spectroscopy and MS analyses (ion trap). Although one resonance is observed in the ^{31}P NMR spectra (Table 1), both **6** and **7** are observed to exist as a mixture of two distinct isomers (**6a**-**7a** / **6b**-**7b**), as determined by ^1H NMR spectroscopy (Figures **S16**–**S24** and Table **S1**). Additionally, ^1H-^1H COSY NMR spectra of the cyclized products (**6**–**7**), allowed for deconvolution of the signals associated to the individual products, with distinctive correlations between the individual ^{i}Pr fragments (Figures **S18** and **S22**). Integration of the ^1H NMR signals from the *p*-cymene ring indicate an isomer ratio of 60:40 for **6** and 87:13 for **7**. In both cases, the major product shows a complete loss of symmetry (as observed by ^1H and $^{13}C\{^1H\}$ NMR spectra) on the *p*-cymene fragment (Figures **S18** and **S22**), with the minor product remaining bilaterally symmetrical [**6a**-**7a** (symmetric) and **6b**-**7b** (asymmetric)]. The diffusion coefficients (D) of **2**, **5** and **7**, determined by DOSY NMR experiments (Table **S1**), allowed for calculation of the hydrodynamic radii. These values are in good agreement with the values obtained from the crystal structures of **2** and **5** and the geometry optimized structures of **7** (*vide infra*). An increase in the hydrodynamic radius is observed between **2** and **5** due to the increased length of the ligand, with only a small change in hydrodynamic radius observed upon cyclization (**7**). Similar to compounds **1**–**5**, scalar spin-spin coupling is observed in the $^{13}C\{^1H\}$ NMR spectra of **6** and **7** between the *p*-cymene and the phosphorus of the PDCA ligand [$^{13}C\{^1H\}$ NMR] [Figure **S22**].[31] With the signals for the non-

quaternary aromatic carbons, in the *p*-cymene fragment, as four distinctive doublets ($^2J_{CP}$ = 3-6 Hz) (Figure **S22**).

The existence of two rotational isomers for compounds **6** and **7** can be explained by the restricted rotation of the *p*-cymene ring. DFT calculations demonstrate the existence of two rotamers, with either the ^{i}Pr (**6a'**/**7a'**) or Me (**6b'**/**7b'**) of the *p*-cymene ring lying above the Cl ligand (Figure 2 and Figures **S26-28**). These rotamers are computed to be close in energy (ΔG = –0.4 kcal mol^{-1} in **6** and –0.2 kcal mol^{-1} in **7**), suggesting minimal thermodynamic preference for either isomer. We propose, therefore, that the product distribution is determined by kinetic control. The strong preference for one isomer in **7** is likely due to a strong conformational preference for complex **5** in solution, which gets "locked in" when the complex cyclises on treatment with a halide abstractor and base. High temperature NMR measurements on **6** and **7** were hindered as the complexes display poor solubility in $CD_3C_6D_5$ and decompose in $CDCl_3$ and CD_3CN. Variable temperature NMR studies (^{1}H and ^{31}P NMR spectroscopy) in CD_2Cl_2 (268–298 K) showed no coalescence, indicating higher temperatures are required for interconversion.

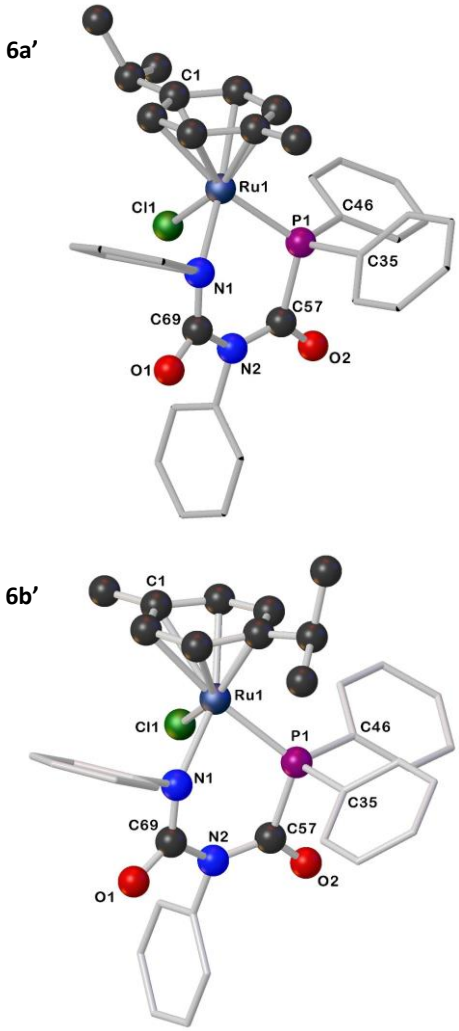


Figure 2. Illustrations for the geometry optimized structures for **6a'** and **6b'**.

Ligand Displacement Studies

To test the stability of the Ru–P bond, solutions of **4** and **5** in CD_2Cl_2 were exposed to an atmosphere of dry CO [Scheme 2 (***B***)]. NMR analysis indicated loss of the PDCA ligands and formation of [{*p*-cymene}$RuCl_2(CO)$][32] (Figure **S25**). Similar behaviour has been observed in $[Rh(\eta^3\text{-TMPP})_2][BF_4]_2$ [TMPP = *tris*(2,4,6-trimethoxyphenyl)phosphine] that when exposed to an atmosphere of CO can reversibly coordinate, a useful feature that has been used for chemosensing applications.[33,34] In contrast, no reaction was observed on treating the metallacycle **6** with CO, suggesting that the chelate complex is more robust to ligand substitution.

Conclusions

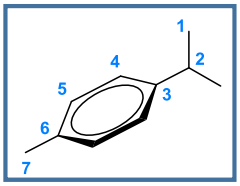
We have described the synthesis of ruthenium(II) complexes coordinated by PCAs and PDCAs, and the first reports of PDCAs as both monodentate and bidentate ligands. In the case of the metallacycles **6** and **7** a mixture of two isomers are obtained; as evidenced by NMR determinations. Whilst the monodentate coordination motif in these complexes can be displaced by CO, chelates **6** and **7** are robust to ligand displacement reactions.

Experimental Section

For full details on experimental procedures, see the Supporting Information.

NOTE: We observed that although compounds **1**-**3** display stability, under aerobic conditions, over the course of a few weeks; samples of **4**-**7** would spontaneously decompose in solution/solid-state even under anoxygenous conditions, over the course of one week.

The phosphine (**L-1** 12 mg; **L-2** 6.9 mg; **L-3** 5.2 mg; **L-4** 6.9 mg; **L-5** 7.4 mg, 0.016 mmol) was dissolved in CD_2Cl_2 (0.4 mL) and added dropwise to a solution of $[Ru(p\text{-cymene})Cl_2]_2$ (5 mg, 8.16×10^{-3} mmol) in CD_2Cl_2 (0.4 mL) with stirring, affording an orange solution. Volatiles were removed under vacuum, affording the target compounds **1**-**5**. In the particular case of **2**, the reaction was successfully scaled up, employing 50 mg (0.08 mmol) of $[Ru(p\text{-cymene})Cl_2]_2$, with full characterization described below.



General numbering scheme for the *p*-cymene fragment for coordination compounds **1**-**5**.

[Ru(*p*-cym){$PPh_2C(=O)N(H)^iPr$}Cl_2] (**1**). ^{1}H NMR δ/ppm (400 MHz, C_6D_6): 8.63 (d, $^3J_{HP}$ = 7.4 Hz, 1H, N*H*), 8.20-8.02 (m, 4H, $PPh_2{}^o$), 7.14-6.94 (m, 6H, $PPh_2{}^{m+p}$), 4.75 (d, $^3J_{HH}$ = 6.1 Hz, 2H, *H*-5), 4.70 (dd, $^3J_{HH}$ = 6.1 Hz, $^3J_{HP}$ = 1.3 Hz, 2H, *H*-4), 4.05 (m, 1H, N^iPr^{CH}), 2.56 (sept, $^3J_{HH}$ = 7.0 Hz, 1H, *H*-2), 1.51 (s, 3H, *H*-7), 1.04 (d, $^1J_{HH}$ = 6.6 Hz, 6H, N^iPr^{CH3}), 0.82 (d, $^3J_{HH}$ = 7.0 Hz, 6H, *H*-1). $^{13}C\{^1H\}$ δ/ppm (400 MHz, C_6D_6): 167.4 (d, $^1J_{CP}$ = 55 Hz, C=O), 134.8 (d, $^2J_{CP}$ = 9 Hz, $PPh_2{}^o$), 133.7 (d, $^1J_{CP}$ = 43 Hz, $PPh_2{}^i$), 130.7 (d, $^4J_{CP}$ = 2 Hz, $PPh_2{}^p$),

128.2 (d, $^3J_{CP}$ = 10 Hz, PPh_2^m), 109.7 (C-6), 95.2 (C-3), 89.7 (d, $^2J_{CP}$ = 4 Hz, C-4), 86.0 (d, $^2J_{CP}$ = 6 Hz, C-5), 43.6 (d, *J* = 6 Hz, N^{i}Pr^{CH}), 30.3 (C-2), 22.2 (C-1), 21.7 (N^{i}Pr^{CH3}), 17.3 (C-7). ^{31}P NMR *δ*/ppm (162 MHz, C_6D_6): 29.8 (s, 1P, Ru*P*Ph$_2$). Anal. Calcd for $C_{26}H_{32}Cl_2NOPRu$: C 54.08, H 5.59, N 2.43; Found C 53.64, H 5.58, N 2.53. HRMS (ESI)$^+$ *m/z*: [M+H]$^+$ calculated 578.0715; found 578.0712 formula $C_{26}H_{33}Cl_2NOPRu$. IR (ATR) $\bar{\nu}_{max}$/cm^{-1}: 3237 (N-H), 1654 (C=O). Red crystalline solid, 5 mg, 39%.

[Ru(*p*-cym){PPh$_2$C(=O)N(*H*)Ph}Cl$_2$] (**2**). ^{1}H NMR *δ*/ppm (400 MHz, CD_2Cl_2): 10.11 (s, 1H, N*H*), 7.88 (ddd, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 1.4 Hz, 4H, PPh_2^m), 7.58 – 7.47 (m, 4H, PPh_2^o), 7.44 (d, $^3J_{HH}$ = 8.4 Hz, 2H, NPh^o), 7.42 – 7.38 (m, 2H, PPh_2^p), 7.21 (t, J = 7.6 Hz, 2H, NPh^m), 7.02 (t, $^3J_{HH}$ = 7.4 Hz, 1H, NPh^p), 5.29 (d, $^3J_{HH}$ = 6.4 Hz, 2H, *H*-5), 5.27 (d, $^3J_{HH}$ = 6.3 Hz, 2H, *H*-4), 2.55 (sept, $^3J_{HH}$ = 7.0 Hz, 1H, *H*-2), 1.84 (s, 3H, *H*-7), 1.04 (d, $^3J_{HH}$ = 7.0 Hz, 6H, *H*-1). ^{13}C{^{1}H} NMR *δ*/ppm (100 MHz, CD_2Cl_2): 167.8 (d, $^1J_{CP}$ = 55 Hz, C=O), 137.0 (NPh^i), 134.7(d, $^3J_{CP}$ = 9 Hz, PPh_2^m), 131.8 (d, $^3J_{CP}$ = 2 Hz, PPh_2^o), 129.9 (PPh_2^i), 129.3 (NPh^m), 129.1(d, $^2J_{CP}$ = 7 Hz, PPh_2^p), 124.9 (NPh^p), 120.3 (NPh^o), 111.0 (C-6), 97.3 (C-3), 90.1 (d, $^2J_{CP}$ = 4 Hz, C-4), 86.9 (d, $^2J_{CP}$ = 5 Hz, C-5), 30.9 (C-2), 22.1 (C-1), 17.9 (C-7). ^{31}P NMR *δ*/ppm (162 MHz, CD_2Cl_2): 37.2 (s, 1P, Ru*P*Ph$_2$). Anal. Calcd for $C_{29}H_{30}Cl_2NOPRu$: C 56.96, H 4.95, N 2.29; Found C 55.48, H 5.01, N 2.30. HRMS/ESI$^+$ *m/z*: [M+Na]$^+$ calculated 634.0383; found 634.0387 formula $C_{29}H_{30}Cl_2NNaOPRu$. IR (ATR) $\bar{\nu}_{max}$/cm^{-1}: 3227 (N-H), 1655 (C=O). Dark red powder, 53 mg, 51%.

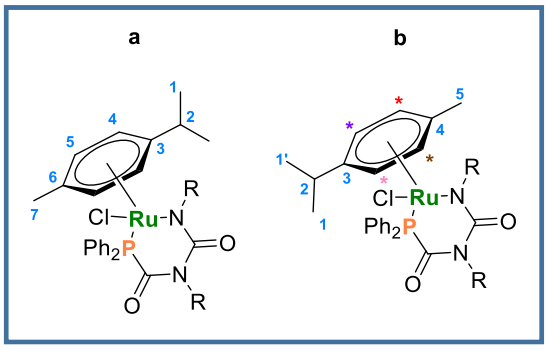
[Ru(*p*-cym){PPh$_2$C(=O)N(*H*)*p*-tol}Cl$_2$] (**3**). ^{1}H NMR *δ*/ppm (400 MHz, CD_2Cl_2): 10.03 (s, 1H, N*H*), 7.90 – 7.84 (m, 4H, PPh_2^o), 7.57 – 7.47 (m, 6H, PPh_2^{m+p}), 7.32 (d, $^3J_{HH}$ = 8.4 Hz, 2H, NPh^m), 7.01 (d, $^3J_{HH}$ = 8.2 Hz, 2H, NPh^o), 5.28 (d, $^3J_{HH}$ = 6.9 Hz, 2H, *H*-5), 5.26 (d, $^3J_{HH}$ = 6.7 Hz, 2H, *H*-4), 2.53 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, *H*-2), 2.24 (s, 3H, NPh$^{CH}{}_3$), 1.83 (s, 3H, *H*-7), 1.03 (d, $^3J_{HH}$ = 7.0 Hz, 6H, *H*-1). ^{13}C{^{1}H} NMR *δ*/ppm (100 MHz, CD_2Cl_2): 167.5 (C=O), 136.2 (NPh$^{CH}{}_3^i$), 134.7 (PPh_2^o), 134.6 (NPh^i), 131.8 (d, $^4J_{CP}$ = 2 Hz, PPh_2^p), 129.7 (NPh^o), 128.9 (d, $^3J_{CP}$ = 10 Hz, PPh_2^m), 120.2 (NPh^m), 110.9 (C-6), 97.2 (C-3), 90.1 (d, $^2J_{CP}$ = 4 Hz, C-4), 86.9 (d, $^2J_{CP}$ = 5 Hz, C-5), 81.4 (d, $^1J_{CP}$ = 70 Hz, PPh_2^i), 30.8 (C-2), 22.1 (C-1), 21.1 (NPh$^{CH}{}_3$), 17.9 (C-7). ^{31}P NMR *δ*/ppm (162 MHz, CD_2Cl_2): 36.6 (s, 1P, Ru*P*Ph$_2$). Anal. Calcd for $C_{30}H_{32}Cl_2NOPRu$: C 57.60, H 5.16, N 2.24; Found C 56.86, H 5.21, N 2.22. HRMS/ESI$^+$ *m/z*: [M-Cl]$^+$ calculated 590.0948, found 590.0961 formula $C_{30}H_{32}ClNOPRu$. IR (ATR) $\bar{\nu}_{max}$/cm^{-1}: 3180 (N-H), 1665 (C=O). Dark red powder, Quantitative yield, 11 mg.

[Ru(*p*-cym){PPh$_2$C(=O)N(Ph)C(=O)N(*H*)Ph}Cl$_2$] (**4**). ^{1}H NMR *δ*/ppm (400 MHz, CD_2Cl_2): 9.25 (s, 1H, N*H*), 7.71 (t, 3H, *J* = 9.0 Hz , *H*-ArP), 7.54 – 7.49 (dd, *J* = 11.8, 7.1 Hz, 2H, *H*-ArN), 7.42 – 7.37 (m, 3H, *H*-ArN), 7.33 – 7.30 (m, 2H, *H*-ArP), 7.26 – 7.05 (m, 9H, *H*-ArN/*H*-ArP), 6.98 (d, *J* = 7.4 Hz, 1H, *H*-ArN), 5.45 (d, $^3J_{HH}$ = 6.0 Hz, 2H, *H*-4), 5.15 (d, $^3J_{HH}$ = 6.0 Hz, 2H, *H*-5), 2.69 (sept, $^3J_{HH}$ = 6.7 Hz, 1H, *H*-2), 1.91 (s, 1H, *H*-7), 1.11 (d, $^3J_{HH}$ = 6.9 Hz, 2H, *H*-1). ^{13}C{^{1}H} NMR *δ*/ppm (100 MHz, CD_2Cl_2): 178.1 (C=O), 177.7 (C=O), 138.2 (d, $^1J_{CP}$ = 9 Hz, PPh_2^i), 134.9 (d, *J* = 9 Hz, ArP), 131.3 (d, *J* = 2.5 Hz, ArP), 129.9 (ArN), 129.8 (ArN), 129.1, 128.7 (NPh^i *x2*), 128.6 (ArN), 128.3 (d, *J* = 10.1 Hz, ArP), 124.7 (ArN), 120.7 (ArN), 120.1 ArN), 110.2 (C-6), 96.9 (C-3), 92.1 (d, $^2J_{CP}$ = 4 Hz, C-4), 86.5 (d, $^2J_{CP}$ = 5 Hz, C-5), 30.7 (C-2), 22.3 (C-1), 17.5 (C-7). ^{31}P NMR *δ*/ppm (162 MHz, CD_2Cl_2): 33.50 (s, 1P, Ru*P*Ph$_2$). Anal. Calcd for $C_{36}H_{35}Cl_2N_2O_2PRu$: C 59.18, H 4.83, N 3.83; Found C 56.48, H 4.73, N 3.67. Despite repeated attempts, a satisfactory elemental analysis for this compound could not be obtained; derived from the aforementioned spontaneous decomposition. HRMS/ESI$^+$ *m/z*: [M-Cl]$^+$ calculated 695.1168, found 695.1158; formula $C_{36}H_{35}ClN_2O_2PRu$. Quantitative conversion as determined by ^{1}H NMR spectroscopy using TMS as internal standard.

[Ru(*p*-cym){PPh$_2$C(=O)N(*p*-tol)C(=O)N(*H*)*p*-tol}Cl$_2$] (**5**). ^{1}H NMR δ/ppm (400 MHz, CD_2Cl_2): 9.20 (s, 1H, NH), 7.68 (t, $^3J_{HH}$ = 9.2 Hz, 4H, PPh_2^m), 7.34 – 7.30 (m, 4H, PPh_2^p), 7.25 (d, $^3J_{HH}$ = 8.5 Hz, 2H, N*H*Ph^m), 7.19 (td, $^3J_{HH}$ = 7.8, $^3J_{HH}$ = 2.0 Hz, 4H, PPh_2^o), 7.05 (d, $^3J_{HH}$ = 8.3 Hz, 2H, N*H*Ph^o), 6.88 (d, $^3J_{HH}$ = 8.2 Hz, 2H, NPh^o), 6.83 (d, $^3J_{HH}$ = 8.4 Hz, 2H, NPh^m), 5.44 (d, $^3J_{HH}$ = 5.4 Hz, 2H, H-4), 5.17 (d, $^3J_{HH}$ = 6.2 Hz, 2H, H-5), 2.70 (sept, $^3J_{HH}$ = 7.0 Hz, 1H, H-2), 2.29 (s, 3H, N*H*Ph$^{CH}{}_3$), 2.24 (s, 3H, NPh$^{CH}{}_3$), 1.90 (s, 3H, H-7), 1.11 (d,

$^{3}J_{HH}$ = 7.0 Hz, 6H, H-1). $^{13}C\{^{1}H\}$ NMR δ/ppm (100 MHz, CD_2Cl_2):177.9 (C=O), 177.5 (C=O), 151.8 (PPh_2^{i}), 138.9 (NPh^{i}), 135.7 ($NHPh^{CH_3 i}$), 135.2 ($NPh^{CH_3 i}$), 135.0 (d, $^{3}J_{CP}$ = 9 Hz, PPh_2^{m}), 134.5 ($NHPh^{i}$), 131.1 (d, $^{4}J_{CP}$ = 3 Hz, PPh_2^{p}), 130.4 (NPh^{o}) 129.7 ($NHPh^{o}$), 128.6 (NPh^{m}), 128.2 (d, $^{2}J_{CP}$ = 10 Hz, PPh_2^{o}), 120.0 ($NHPh^{m}$), 110.1 (C-6), 96.9 (C-3), 92.1 (d, $^{2}J_{CP}$ = 4 Hz, C-4), 86.5 (d, $^{2}J_{CP}$ = 6 Hz, C-5), 30.8 (C-2), 22.3 (C-1), 21.3 (NPh^{CH_3}), 21.1 ($NHPh^{CH_3}$), 17.45 (C-7). ^{31}P NMR δ/ppm (162 MHz, CD_2Cl_2): 33.76 (s, 1P, $RuPPh_2$). Anal. Calcd for $C_{38}H_{39}Cl_2N_2O_2PRu$: C 60.16, H 5.18, N 3.69; Found C 60.12, H 5.43, N 3.20. HRMS/ESI^{+} *m/z*: $[M\text{-}Cl]^{+}$ calculated 723.1476, found 723.1489; formula $C_{38}H_{39}ClN_2O_2PRu$. Quantitative conversion by NMR using TMS as internal standard.

Typical procedure for the formation of metallacycles **6** and **7**. A solution containing **4** or **5** (0.016 mmol) in CD_2Cl_2 (0.6 mL) was added to a mixture of K_2CO_3 (6.8 mg, 0.048 mmol) and $AgPF_6$ (5.4 mg, 0.02 mmol) (as solids), and transferred to a J. Young's tap NMR tube. The heterogeneous mixture was agitated *via* sonication at room temperature for 10 minutes, and filtered, affording an orange-red solution. Removal of volatiles *in vacuo* afforded full conversion to the cyclized products **6** and **7**, respectively. Quantitative conversion was determined by ^{1}H NMR spectroscopy using TMS as internal standard.



General numbering scheme for cyclization compounds **6** and **7**.

[Ru(*p*-cym){κ^2-*P,N*-PPh_2C(=O)N(Ph)C(=O)NPh}Cl] (**6**). Mixture of 2 products, ratio 60:40. (**6b** as main product) Characterization for **6a** and **6b**: ^{1}H NMR δ/ppm (400 MHz, CD_2Cl_2): 7.81-7.71 (m, Ph), 7.66-7.63 (m, 2H, Ph), 7.58-7.53 (m, Ph), 7.51 (d, *J* = 7.7 Hz, 6H, NPh), 7.47-7.37 (m, Ph), 7.23 (d, *J* = 7.6 Hz, 4H, NPh), 7.03 (s, 2H, Ph), 5.69-5.62 (m, 4H, **6b**-^{i}Pr-C_6H_4-Me), 5.64 (d, $^{3}J_{HH}$ = 6.1 Hz, 2H, **6a**-H5), 5.46 (d, $^{3}J_{HH}$ = 6.1 Hz, 2H, **6a**-H4), 2.78 (sept, *J* = 6.8 Hz, 1H, **6a**-H2), 2.21 (s, 3H, **6a**-H7), 1.85 (sept, *J* = 6.86 Hz, 1H, **6b**-H2), 1.64 (s, 3H, **6b**-H5), 1.30 (d, *J* = 6.9 Hz, 6H, **6a**-H1), 0.83 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, **6b**-H1), 0.78 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, **6b**-H1'). $^{13}C\{^{1}H\}$ NMR δ/ppm (100 MHz, CD_2Cl_2): 135.4 (d, *J* = 11 Hz, Ph), 134.3 (d, *J* = 36 Hz, Ph), 133.9 (d, *J* = 2 Hz, Ph), 133.7 (d, *J* = 10.1 Hz, Ph), 131.7 (d, *J* = 20 Hz, Ph), 130.9 (d, *J* = 10 Hz, Ph), 130.1 (NPh), 129.4 (d, *J* = 11 Hz, Ph), 129.2 (d, *J* = 11 Hz, Ph), 126.5 (NPh), 108.8 (**6b**-C4), 102.4 (**6a**-C6), 97.7 (**6a**-C3), 97.3 (**6b**-C3), 90.5 (d, $^{2}J_{CP}$ = 3 Hz, **6b**-^{i}Pr-C_6H_4-Me), 88.3 (d, $^{2}J_{CP}$ = 6 Hz, **6b**-^{i}Pr-C_6H_4-Me), 87.2 (d, $^{2}J_{CP}$ = 3 Hz, **6b**-^{i}Pr-C_6H_4-Me), 85.6 (d, $^{2}J_{CP}$ = 4 Hz, **6b**-^{i}Pr-C_6H_4-Me), 79.4 (**6a**-C5), 78.6 (**6a**-C4), 31.9 (**6a**/**6b**-C2), 22.2 (**6b**-C1), 21.4 (**6a**-C1), 20.9 (**6b**-C1'), 19.3 (**6a**-C7), 17.9 (**6b**-C5). ^{31}P NMR δ/ppm (162 MHz, CD_2Cl_2): 52.59 (s, 1P, $RuPPh_2$). HRMS/ESI^{+} *m/z*: $[M+H]^{+}$ calculated 695.1168, found 695.1175; formula $C_{36}H_{35}ClN_2O_2PRu$. IR (ATR) $\bar{\nu}_{max}$/cm^{-1}: 1616 (C=O), 1584 (C=O). Dark orange powder, 10 mg, 88%.

[Ru(*p*-cym){κ^2-*P,N* PPh_2C(=O)N(*p*-tol)C(=O)N*p*-tol}Cl] (**7**). Mixture of 2 products, ratio 87:13. (**7b** as main product). Characterization for **7b**: ^{1}H NMR δ/ppm (400 MHz, CD_2Cl_2): 7.80-7.70 (m, 7H, *H*-ArP), 7.64 (tq, *J* = 7.5, 2.04 Hz, 1H, *H*-ArP), 7.53 (td, *J* = 7.6, 3.0 Hz, 2H, *H*-ArP), 7.33 (t, $^{3}J_{HH}$ = 8.1 Hz, 5H, *H*-

ArN), 7.10 (d, $^{3}J_{HH}$ = 8.3 Hz, 3H, *H*-ArN), 5.64-5.69 (m, 3H, ^{i}Pr-C$_6$*H*$_4$-Me), 5.62 (d, $^{3}J_{HH}$ = 6.3 Hz, 1H, ^{i}Pr-C$_6$*H*$_4$-Me), 2.42 (s, 3H, *H*6), 2.39 (s, 3H, *H*7), 1.85 (sept, $^{3}J_{HH}$ = 6.9 Hz, 1H, *H*2), 1.65 (s, 3H, *H*5), 0.84 (d, $^{3}J_{HH}$ = 7.0 Hz, 3H, *H*1), 0.79 (d, $^{3}J_{HH}$ = 7.0 Hz, 3H, *H*1'). ^{13}C{^{1}H} NMR δ/ppm (100 MHz, CD_2Cl_2): 170.9 (d, $^{1}J_{CP}$ = 51 Hz, Ph_2P-C=O), 162.1 (d, $^{3}J_{CP}$ = 3 Hz, C=O), 142.5 (quat-N), 139.6 (quat-N), 135.4 (d, *J* = 11 Hz, ArP), 133.8 (d, *J* = 3 Hz, ArP), 133.6 (d, *J* = 10 Hz, ArP), 132.2 (quat-N), 131.4 (ArN), 130.8 (d, *J* = 10 Hz, ArP), 130.5 (quat-N), 129.4 (d, *J* = 11 Hz, ArP), 127.1 (d, *J* = 45 Hz, ipso-P), 126.3 (d, *J* = 51 Hz, ipso-P), 126.2 (ArN), 108.8 (d, $^{2}J_{CP}$ = 2 Hz, C4), 97.1 (C3), 90.6 (d, $^{2}J_{CP}$ = 4 Hz, ^{i}Pr-*C*$_6$H$_4$-Me), 88.1 (d, $^{2}J_{CP}$ = 6 Hz, ^{i}Pr-*C*$_6$H$_4$-Me), 87.1 (d, $^{2}J_{CP}$ = 2 Hz, ^{i}Pr-*C*$_6$H$_4$-Me), 85.6 (d, $^{2}J_{CP}$ = 4 Hz, ^{i}Pr-*C*$_6$H$_4$-Me), 31.1 (C2), 22.1 (C1), 21.5 (C7), 21.4 (C-6), 20.8 (C1'), 17.9 (C5). ^{31}P NMR δ/ppm (162 MHz, CD_2Cl_2): 52.34 (s, 1P, Ru*P*Ph$_2$). HRMS/ESI^{+} *m/z*: $[M+H]^{+}$ calculated 723.1476, found 723.1477; formula $C_{38}H_{39}ClN_2O_2PRu$. IR (ATR) $\bar{\nu}_{max}$/cm^{-1}: 1594 (C=O), 1509 (C=O). Dark orange powder, 10 mg, 85%.

Typical procedure for reactivity with CO. An NMR tube containing a solution of **4** (0.016 mmol) in 0.6 mL of CD_2Cl_2, was charged with an atmosphere of CO *via* three freeze-thaw cycles. The resulting sample was studied *via* multinuclear NMR spectroscopies [^{1}H, ^{13}C{^{1}H} and ^{31}P NMR]; showing formation of the corresponding free phosphine/PDCA (**L-4**) and [{*p*-cymene}$RuCl_2$(CO)], in accordance with the reported literature.[9,32]

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Conflicts of interest

There are no conflicts to declare.

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