Synthesis, Structure, Reactivity, and Electrochemical Study of a (2,2′-Biphosphinine)(η^5-pentamethylcyclopentadienyl)chlororuthenium(II) Complex

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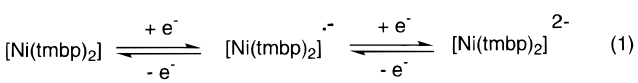
Received January 31, 1996[⊗]

[RuCp*(η^4-C_6H_{10})Cl] (Cp* = C_5Me_5; **1**) reacts with the tmbp ligand (**2**; tmbp = 4,4′,5,5′-tetramethyl-2,2′-biphosphinine) in THF to afford the [RuCp*(tmbp)Cl] complex **3**, which has also been characterized by a single-crystal X-ray diffraction study. Complex **3** crystallizes with one THF molecule. The environment about the Ru atom corresponds to that of a classical three-legged piano-stool structure. Reaction of **3** with LiBr and KCN in CH_2Cl_2/MeOH afforded [RuCp*(tmbp)Br] (**4**) and [RuCp*(tmbp)CN] (**5**), respectively. **3** also reacts in CH_2Cl_2, in the presence of NH_4PF_6, with various monodentate ligands to produce a series of stable cationic complexes of the type [RuCp*(tmbp) (L)]$^+$[PF_6]$^-$ (L = acetonitrile (**6**), pyridine (**7**), trimethyl phosphite (**8**), triphenylphosphine (**9**), 2-bromo-4,5-dimethylphosphinine (**10**), *tert*-butyl isocyanide (**11**), *cis*-cyclooctene (**12**), norbornene (**13**)). All complexes were obtained in good yields and have been characterized by a combination of elemental analyses and spectroscopic methods (IR and ^{31}P, ^{1}H, and ^{13}C NMR). The redox chemistry of **3** has been investigated by cyclic voltammetry in MeCN. Complex **3** is reversibly oxidized in [RuCp*^{III}(tmbp)Cl] at +0.49 V (vs SCE). The first irreversible monoelectronic reduction wave, which occurs at −1.82 V vs SCE, indicates the formation of the [Ru^{I}Cp*(tmbp)] complex with the loss of Cl^-. The second reversible reduction wave at −2.24 V was assigned to the formation of the anionic [Ru^{0}Cp*(tmbp)]$^-$ complex, which is stable within the time scale of the cyclic voltammetry.

Introduction

It is now well-established that the field of interest of 2,2′-biphosphinines in coordination chemistry will be markedly different from that of classical tertiary diphosphines and 2,2′-bipyridines.[1] Due to a suitable balance between their poor σ-donor and their strong π-accepting power, they act as powerful chelate ligands for the stabilization of electron-excessive metal centers. Recently, we demonstrated that point in the case of an electrochemically reduced (tmbp)$_2$ Ni^0 complex[2a] (tmbp = 4,4′,5,5′-tetramethyl-2,2′-biphosphinine)[3] (eq 1).



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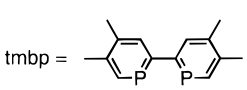
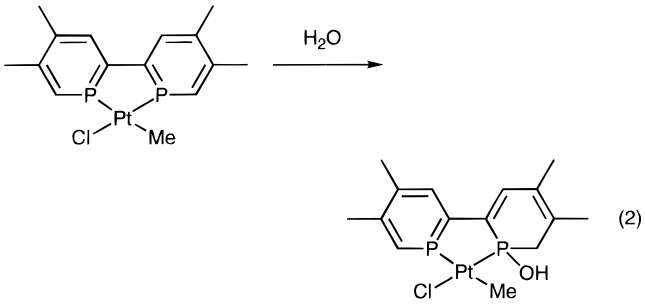


On the other hand, their coordination chemistry toward metallic centers having a positive oxidation state (essentially +2) still remains unclear and from a previous report it appears that, in some cases, complexes are less stable. Upon complexation, the aromaticity of the ligand is disrupted and the phosphinine nucleus behaves as a genuine cyclophosphahexatriene with a highly reactive P=C double bond. The following example of a Pt(II) complex is highly illustrative. In the presence of traces of water, a selective addition of water to the P=C_6 double bond of the phosphinine ring *trans* to the less electron donating ligand is observed[4] (eq 2).



(2)

This reactivity is not specific to biphosphinines, and similar reactions have also been observed by Venanzi's

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1996.

(1) Mathey, F.; Le Floch, P. *Chem. Ber.*, in press.

(2) (a) Le Floch, P.; Ricard, L.; Mathey, F.; Jutand, A.; Amatore, C. *Inorg. Chem.* **1995**, *34*, 5070. (b) Several homoleptic complexes of zerovalent metals having the parent phosphinine C_5H_5P as a ligand have been synthesized; see: Elschenbroich, C.; Nowotny, M.; Behrendt, A.; Massa, W.; Wocaldo, S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1343. Elschenbroich, C.; Nowotny, M.; Kroker, J.; Behrendt, A.; Massa, W.; Wocaldo, S. *J. Organomet. Chem.* **1993**, *459*, 157. Elschenbroich, C.; Nowotny, M.; Behrendt, A.; Harms, K.; Wocaldo, S.; Pebler, J. *J. Am. Chem. Soc.* **1994**, *116*, 6217.

S0276-7333(96)00063-5 CCC: $12.00

group during their studies on the coordination chemistry of the 2-(2-pyridyl)-4,5-dimethylphosphinine ligand (NIPHOS) with Pt(II) and Pd(II) cationic centers.[5]

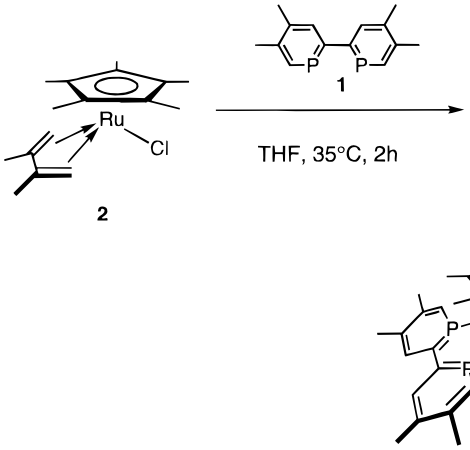
More convincing results have been obtained with Ru(II) centers, for which two biphosphinine complexes, *cis*-$[Ru(tmbp)(dmso)_2Cl_2]$ and *cis*-$[Ru(tmbp)_2Cl_2]$, have been characterized[6] by us in 1992. Nevertheless, during a preliminary investigation of their reactivity, we found that the stability of their cationic derivatives was dramatically dependent on the nature of the ancillary ligands. The first series of experiments aiming to synthesize biphosphinine analogs of the $[Ru(bpy)_3]^{2+}$ dication showed us that the stability of complexes increased with the number of bipyridine ligands. In that way, whereas the instability of the two dications $[Ru(tmbp)_3]^{2+}[BF_4]^-_2$ and $[Ru(tmbp)_2(bpy)]^{2+}[BF_4]^-_2$ prevented any characterizations, the $[Ru(tmbp)(bpy)_2]^{2+}$-$[BF_4]^-_2$ complex was found to be rather stable.[7]

The different factors which govern the stability of complexed biphosphinines have not been totally rationalized thus far; nevertheless, it is quite clear that the electron density available at the metal center plays a decisive role in providing (or not) sufficient π backdonation within the π^* delocalized system of the ligand. To confirm this hypothesis, we decided to explore the synthesis and the chemistry of very electron-rich cationic ruthenium(II) complexes and, quite logically, we focussed our study on the RuCp* fragment, which is probably the best prototype. Besides the theoretical information provided by this study, we also found that it might be of interest to appreciate to what extent the Lewis acidic character of this electron-rich fragment can be modulated by a strongly π accepting chelate ligand. Indeed, the chemistry of $[RuCp^*L_2X]$ complexes has been essentially studied so far with good σ-donor ligands. In this paper, we report the synthesis and an electrochemical study of the [RuCp*(tmbp)Cl] complex, as well as some studies on its reactivity.

Results and Discussion

(i) Synthesis and Structure of [RuCp*(tmbp)Cl].

Several approaches have been devised for the synthesis of $[RuCp^*L_2Cl]$ complexes (L = phosphorus or nitrogen 2e$^-$ donor ligands). These include the reaction of L with the $[RuCp^*Cl_2]_n$[8] polymer in the presence of a reducing agent[9] or with the tetrameric $[RuCp^*(\mu_3\text{-}Cl)]_4$ complex[10] and the traditional ligand exchange with $(\eta^2\text{-olefin})_2$ or $[RuCp^*(\eta^4\text{-diene})Cl]$ complexes.[11] All these methods were attempted with the tmbp ligand **1**. Surprisingly, the reaction of **1** with the $[RuCp^*Cl_2]_n$ polymer/Zn mixture in THF at room temperature did not proceed cleanly and the expected Cp*Ru(tmbp)Cl complex **3** was only formed in low yields (<30%) along with other unidentified biphosphinine complexes. The reaction of **1** with the tetrameric $[RuCp^*(\mu_3\text{-}Cl)]_4$ in THF at 25 °C afforded **3** in 60% yield. Finally, the best fit was obtained using the precursor $[RuCp^*(\eta^4\text{-DMB})Cl]$[10d] (DMB = 2,3-dimethyl-1,3-butadiene), which was prepared directly from the $[RuCp^*Cl_2]_n$ polymer by a reductive procedure (see Experimental Section). The substitution of the diene was performed in THF at 35 °C and gave complex **3** in 85% yield (eq 3).



(3)

Complex **3** was isolated as a red-brown powder, air stable in the solid state for long periods, soluble in CH_2Cl_2 and acetone, moderately soluble in THF and alcohols, and insoluble in ether and petroleum ether. In ^{31}P NMR, the complexation induces a strong downfield shift ($\delta(CDCl_3)$ 224.60 ppm for **3** *vs* $\delta(CDCl_3)$ 178.32 ppm for the free ligand **1**). As expected, **3** presents a good resistance toward hydrolysis and no reaction was observed at the complexed P=C double bonds upon treatment with water and alcohols in dichlromethane at 30 °C for hours. Fortunately, we were able to grow crystals of **3** by cooling a THF/pentane (1:1) solution at −20 °C.

The molecular structure of **3** has been determined by a single-crystal X-ray diffraction study. An ORTEP view of the molecule is presented in Figure 1. Selected bond distances and angles are given in Table 1. The environment about the Ru atom corresponds to that of a classical three-legged piano-stool structure. Interesting structural features of this complex are the two Ru−P bond distances. As expected for a strong π-acceptor ligand, these two bonds (Ru−P1 = 2.2475(7) Å and Ru−P12 = 2.2375(7) Å) are clearly short when compared to those observed for classical tertiary phosphines, which usually are in the range 2.30−2.35 Å in $[RuCp^*(R_3P)_2L]$ neutral or cationic complexes.[11,12] Besides, the distance

(3) (a) Le Floch, P.; Carmichael, D.; Ricard, L.; Mathey, F. *J. Am. Chem. Soc.* **1991**, *113*, 667. (b) Le Floch, P.; Carmichael, D.; Ricard, L.; Mathey, F.; Jutand, A.; Amatore, C. *Organometallics* **1992**, *11*, 2475. (c) Le Floch, P.; Ricard, L.; Mathey, F. *Bull. Soc. Chim. Fr.* **1994**, *131*, 330.

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(5) Schmid, B.; Venanzi, L. M.; Gerfin, T.; Gramlich, V. Mathey, F. *Inorg. Chem.* **1992**, *31*, 5117.

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(12) See for example: (a) Lindner, E.; Haustein, M.; Fawzi, R.; Steimann, M.; Wegner, P. *Organometallics* **1994**, *13*, 5021. (b) Le Lagadec, R.; Roman, E.; Toupet, L.; Müller, U.; Dixneuf, P. H. *Organometallics* **1994**, *13*, 5030. (c) Bruce, M. I.; Humphrey, M. G.; Patrick, J. M.; White, A. H. *Aust. J. Chem.* **1983**, *36*, 2065.

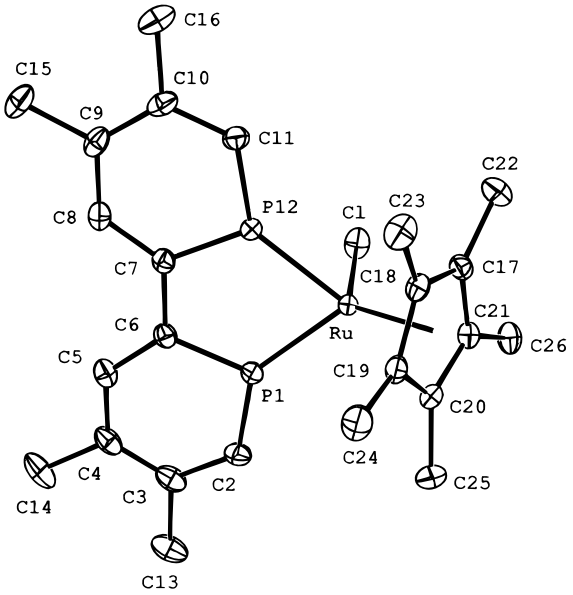


Figure 1. ORTEP drawing of one molecule of **3**. Ellipsoids are scaled to enclose 50% of the electron density. The crystallographic labeling is arbitrary and different from the numbering used for assignment of the ^{13}C spectra.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 3[a]

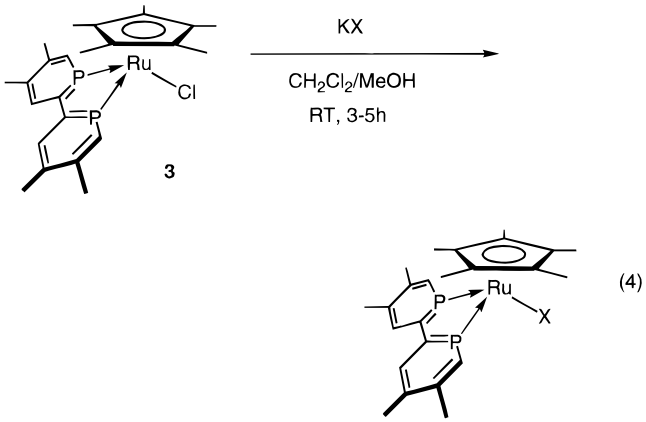
	Bond Lengths		
Ru−Cl	2.4538(7)	Ru−Ct	1.852(3)
Ru−P1	2.2475(7)	Ru−P12	2.2375(7)
P1−C2	1.712(3)	P12−C11	1.707(3)
C2−C3	1.408(4)	C11−C10	1.397(4)
C3−C4	1.386(5)	C10−C9	1.402(4)
C4−C5	1.392(4)	C9−C8	1.400(4)
C5−C6	1.391(4)	C8−C7	1.393(4)
C6−P1	1.740(3)	C7−P12	1.730(3)
C6−C7	1.466(4)		
	Bond Angles		
P1−Ru−P12	78.45(3)	Cl−Ru−Ct	120.1
P1−Ru−Ct	131.0	P12−Ru−Ct	130.5
P1−C2−C3	123.4(2)	Cl−Ru−P1	93.88(3)
C2−C3−C4	123.0(3)	Cl−Ru−P12	89.77 (3)
C3−C4−C5	123.0(3)	P1−C6−C7	113.1(2)
C4−C5−C6	125.4(3)	Ru−P1−C6	117.3(1)
C5−C6−P1	121.1(2)	Ru−P1−C2	138.7(1)
C6−P1−C2	104.1(1)	C7−P12−C11	104.7(1)

[a] Ct = centroid of the Cp* ligand.

from the ruthenium atom to the Cp* plane (1.852(3) Å) and the Ru−Cl bond length (2.4538(7) Å) appear quite normal.[12]

Some additional interesting information is provided by the intramolecular bond length and angle values within the biphosphinine ligand. From these, it appears that no dearomatization takes place in each ring, as demonstrated, for example, by the good homogeneity of the C−C double-bond lengths (between 1.386(5) and 1.408(4) Å; see Table 1). Additionally, as we previously noted,[2a] the opening of the intracyclic ∠CPC angle, which can be correlated with the electron-accepting character of the metallic fragment, is another important piece of data which finely reflects the loss of aromaticity in a complexed phosphinine. In complex **3** this value (average of ∠C2−P1−C6 and ∠C7−P12−C11 104.4°) is almost identical with that observed in the [Cr(tmbp)-$(CO)_4$] complex (104.3°),[3a] which is highly stable. For comparison, in the less stable *cis*-[Ru(tmbp)$(dmso)_2Cl_2$] complex,[6] the opening of the ∠CPC angle is 106.08°.

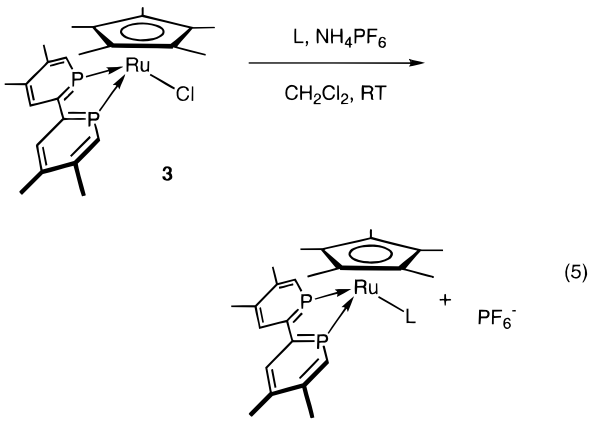
(ii) Reactivity of [(tmbp)RuCp*Cl] (3). In order to appreciate the influence of the biphosphinine ligand on the chemistry of the RuCp*Cl fragment, it seemed worthwhile to explore in a first step the reactivity of the Ru−Cl bond in **3** with regard to substitution reactions. Owing to the good stability of **3** in alcohols, we first investigated the metathesis of this bond with KBr and KCN. These two reactions proceeded in a CH_2-Cl_2/MeOH mixture at room temperature and gave complexes **4** (X = Br) and **5** (X = CN) in good yields (eq 4). As we previously noted for **3**, no side reactions



(4)

(addition of MeOH) were observed at the complexed P═C bonds of **4** and **5** during the reaction, thus confirming their stability.

We also investigated the substitution of the Ru−Cl bond with various monodentate ligands such as acetonitrile, pyridine, phosphines (PPh_3 and $P(OMe)_3$), 2-bromo-4,5-dimethylphosphinine, *tert*-butyl isocyanide, and olefins (*cis*-cyclooctene and norbornene). All these reactions were conducted in CH_2Cl_2 at room temperature in the presence of NH_4PF_6 to facilitate the displacement of the chlorine ligand. As does their precursor **3**, complexes **6**−**13**, which were isolated in moderate to good yields, show a good stability in solution and are not moisture sensitive. All these results are summarized in eq 5.



(5)

6, L = NCMe (80%) **10**, L = C_7H_8PBr (85%)
7, L = Py (75%) **11**, L = CN^tBu (65%)
8, L = $P(OMe)_3$ (80%) **12**, L = cis-C_8H_{14} (50%)
9, L = PPh_3 (80%) **13**, L = C_7H_{10} (70%)

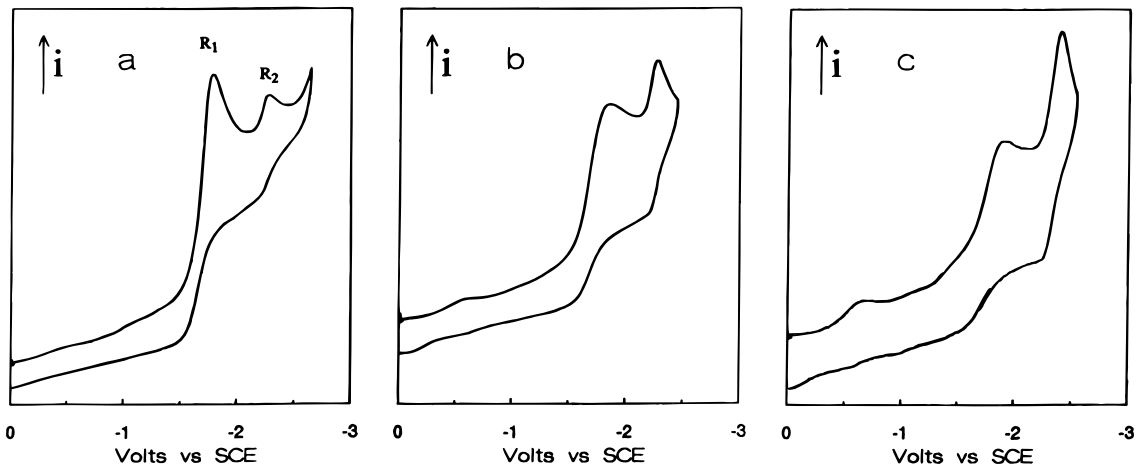


Figure 2. Cyclic voltammetry of **3** (2 mM) in MeCN containing *n*-Bu_4NBF_4 (0.3 M) at a stationary gold-disk microelectrode (0.5 mm diameter) and 20 °C. Scan rate: (a) 0.5 V s^{-1}; (b) 2 V s^{-1}; (c) 10 V s^{-1}.

Complexes **6**−**13**, which have been isolated as crystalline solids, readily soluble in CH_2Cl_2, were succesfully characterized by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy and elemental analysis in most cases. Additionally, complex **11** was also identified by IR spectroscopy (ν(NC) in CCl_4 2143 cm^{-1}),[13] since the quaternary carbon of the isocyanide ligand could not be detected in the ^{13}C NMR spectrum. For complexes **12** and **13**, the η^2 coordination of the olefin is evidenced in ^{13}C NMR by the strong shift toward high field observed for the two olefinic carbon atoms (δ (CD_2Cl_2) in ppm 74.80 in **12** and 67.95 in **13**, compared to 130.2 and 135.8 in the free ligands, respectively).

The formation of these two complexes is of particular interest when we refer to the work on the very electron rich $[RuCp^*(bpy)]^+$ fragment published by Balavoine et al.[14] During their investigation, they found that the presence of the strong σ-donor bipyridine ligand strongly disfavored the coordination of electron-rich olefins at the Ru center, whereas complexes with olefins bearing electron-withdrawing groups were found to be stable. In contrast, with the $[RuCp^*(tmbp)]^+$ unit, whereas complexes **12** and **13** were easily formed, derivatives with methyl acrylate and diethyl maleate were too labile to be isolated. This difference in the reactivty of the two complexes, which cannot be rationalized in terms of steric demand since the two ligands have nearly the same geometry, nicely illustrates the increase of the Lewis acidic character of the metal induced by the coordination of the biphosphinine.

(iii) Electrochemical Study of [RuCp*(tmbp)Cl] (3). The cyclic voltammetry of **3** (2 mM) in MeCN containing *n*-Bu_4NBF_4 (0.3 M) was performed at a stationary gold-disk electrode with a scan rate of 0.2 V s^{-1}. First, to complete our comparison between biphosphinine and bipyridine complexes, we investigated the oxidation of **3**. A reversible oxidation peak, which is assigned to the formation of the Ru^{III} complex, was observed at $E^p_{O1} = +0.49$ V *vs* SCE (eq 6).

$$[Ru^{II}Cp^*(tmbp)Cl] \underset{}{\overset{-1\ e^-}{\rightleftharpoons}} [Ru^{III}Cp^*(tmbp)Cl]^+ \qquad \text{reversible at } O_1 \qquad (6)$$

As expected, this value is shifted anodically with respect to the oxidation potential of the [RuCp*(bpy)-Cl] complex ($E_{1/2} = 0.07$ V *vs* SCE in CH_2Cl_2),[15] thus confirming that the ruthenium center is more electron deficient in **3**.

In view of the good ability of the biphosphinine ligand to accept and delocalize electron density, we focused our study on the electrochemical reduction of **3** to find out whether low-valent ruthenium complexes could be viable or not.

The cyclic voltammogram exhibited two reduction peaks with different magnitudes (Figure 2a). The first irreversible peak was observed at $E^p_{R1} = -1.82$ V *vs* SCE. The second one, of smaller magnitude, was reversible and was observed at $E^p_{R1} = -2.24$ V. A determination of the absolute number of electrons involved in the first reduction peak[16] at long time (0.2 s) revealed that two electrons were involved in the first electrochemical process.

Increasing the scan rate resulted in a decay of the first reduction peak current while the second one increased (Figure 2b). At high scan rate (above 10 V s^{-1}), the magnitudes of the two peaks were found to almost be similar (Figure 2c), indicating that the same numbers of electrons were involved in the two successive electrochemical processes. The first reduction peak remained irreversible in the range of scan rate investigated here. Plotting the variation of the reduction peak current of R_1 as a function of the scan rate showed that the initial two-electron transfer (taking place at long time) evolved toward a one-electron transfer at short time.[17] Therefore, at high scan rate, two one-electron transfers were observed that are consistent with the mechanism given in eqs 7 and 8.

$$[Ru^{II}Cp^*(tmbp)Cl] \underset{}{\overset{+1\ e^-}{\longrightarrow}} [Ru^{I}Cp^*(tmbp)] + Cl^- \qquad \text{irreversible at } R_1 \qquad (7)$$

3

$$[Ru^{I}Cp^*(tmbp)] \underset{}{\overset{+1\ e^-}{\rightleftharpoons}} [Ru^{0}Cp^*(tmbp)]^- \qquad \text{reversible at } R_2 \qquad (8)$$

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(14) Balavoine, G. G. A.; Boyer, T.; Livage, C. *Organometallics* **1992**, *11*, 456.
(15) Koelle, U.; Kossakowski, J. *Inorg. Chim. Acta* **1989**, *164*, 23.

At low scan rate, wave R_1 remained chemically irreversible yet and the magnitude of the second peak R_2 was smaller than half the value of that of the first one, indicating that the complex [Ru^ICp^*(tmbp)] was involved in a chemical reaction during the time elapsed between R_1 and R_2. This reaction provoked a decay of the concentration of [Ru^ICp^*(tmbp)] in the diffusion layer, and only the reduction of the [Ru^ICp^*(tmbp)] which had not completely reacted was observed at R_2. This chemical reaction of [Ru^ICp^*(tmbp)], probably with a Ru^{II} complex, affords a binuclear complex. The fact than more than one electron was involved at long time, in the first electrochemical step, suggests that the binuclear complex is more easily reduced than [$Ru^{II}Cp^*$-(tmbp)Cl]. To support the formation of this binuclear complex, cyclic voltammetry was performed at different scan rates on solutions of [$Ru^{II}Cp^*$(tmbp)Cl] of various concentrations. Plotting the variation of the peak current of R_1 as a function of log(v/[$Ru^{II}Cp^*$(tmbp)Cl]) (Figure 3) resulted in a single curve, demonstrating that the overall reaction order in ruthenium centers in the chemical step was 2 and therefore that a reaction between two ruthenium complexes took place with a rate constant in the range of 10^4 M^{-1} s^{-1}. The mechanism given by eqs 9 and 10 can be tentatively proposed to rationalize the formation of this $Ru^{II}-Ru^I$ dimer and its monoelectronic reduction.

$$\underset{\mathbf{3}}{[Ru^{II}Cp^*(tmbp)Cl]} + [Ru^ICp^*(tmbp)] \longrightarrow [Cp^*(tmbp)Ru^{II}\!\!-\!\!Ru^ICp^*(tmbp)]^+Cl^- \quad (9)$$

$$[Cp^*(tmbp)Ru^{II}\!\!-\!\!Ru^ICp^*(tmbp)]^+Cl^- \xrightarrow{+\,1\,e^-} [Cp^*(tmbp)Ru^I\!\!-\!\!Ru^ICp^*(tmbp)] + Cl^- \quad (10)$$

In conclusion, the irreversibilty of the first reduction peak R_1 at high scan rates, even when the bimolecular reaction was not operating, means that a fast chemical step takes place after the first electron transfer. This observation is in good agreement with a fast cleavage of the Ru−Cl bond (as proposed in eq 7) from the anion radical complex $[Ru^{II}Cp^*(tmbp)Cl]^{\bullet -}$ formed upon the first electron transfer. On the other hand, the good reversibility of the second reduction peak R_2, even at long time (at least over 2 s), demonstrates the stability of the Cp^*Ru^0(tmbp) anion. Such anionic species are not totally unprecedented. In 1990, Fagan et al. showed that [RuCp*(η^4-diene)] and [RuCp*(η^2-C_2H_4)$_2$]$^-$[Li·DME]$^+$ complexes could be isolated.[10d]

Conclusion

In this paper, we have shown that the stability of a complexed biphosphinine on a Ru(II) center is clearly dependent on the nature of the ancillary ligands. With a powerful electron-releasing ligand such as $C_5Me_5^-$, the easily available chlorine complex [RuCp*(tmbp)Cl] (**3**) shows a remarkable stability and can be used as an efficient precursor for the synthesis of various cationic complexes of the type [RuCp*(tmbp)L]$^+$[PF_6]$^-$. As expected, the strong π-accepting character of the biphosphinine ligand increases the Lewis acid character of the Ru^+Cp^* fragment which coordinates electron-rich olefins, in contrast to its bipyridine counterpart. The electrochemical behavior of complex **3** has also been investigated. This study reveals that, upon reduction with one electron, the Ru−Cl bond rapidly dissociates, leading to a [Ru^ICp^*(tmbp)] complex which can be reduced at a more negative potential to give the stable anion [Ru^0Cp^*(tmbp)]$^-$.

In conclusion, these preliminary encouraging results demonstrate that the biphosphinine ligand might be succesfully used to stabilize various oxidation states with RuCp* complexes (from +3 to 0). Investigations are underway in our laboratory to further extend this chemistry to other electron-rich neutral and cationic centers.

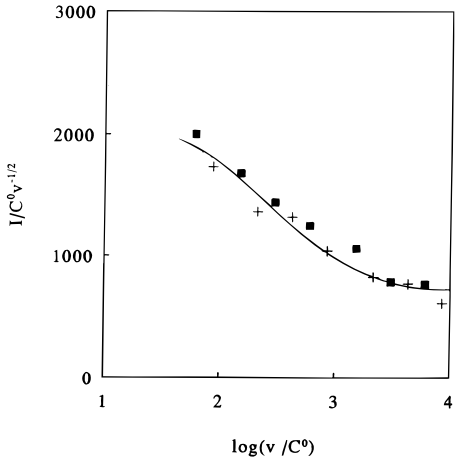

Figure 3. Variation of $I/C^0v^{-1/2}$ (I = reduction current of R_1; v = scan rate; C^0 = [RuCp*(tmbp)Cl]) as a function of log(v/C^0).

Experimental Section

All reactions were routinely performed under an inert atmosphere of either nitrogen or argon by using Schlenk techniques and dry deoxygenated solvents. Dry THF, ether, toluene, and hexane were obtained by distillation from Na/benzophenone, dry CH_2Cl_2 was obtained by distillation from P_2O_5, and dry MeCN and pyridine were obtained by distillation over CaH_2. Dry Celite was used for filtration. Nuclear magnetic resonance spectra were obtained on a Bruker AC-200 SY spectrometer operating at 200.13 MHz for ^1H, 50.32 MHz for ^{13}C, and 81.01 MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from external TMS (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P), and coupling constants are given in hertz. The following abreviations are used: s, singulet; d, doublet; t, triplet; q, quadruplet; sept, septuplet; m, multiplet; b, broad; v, virtual). Elemental analyses were performed by the "Service d'analyse du CNRS", at Gif-sur-Yvette, France. [RuCp*Cl_2]$_n$ was prepared according to ref 7b. Preparation of [RuCp*(η^4-C_6H_{10})Cl] was carried out by modifications of reported methods.[18]

Preparation of [RuCp*(η^4-C_6H_{10})Cl] (2). Zinc powder (6.0 g, 91.5 mmol) was added to a solution of [RuCp*Cl_2]$_n$ (6.0 g, 19.55 mmol) and 2,3-dimethyl-1,3-butadiene (8.00 g, 97.60

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(17) In Figure 3, the limit at high scan rate appears smaller than half the value at low scan rates. This occurs because the wave R_1 is then partially controlled by the kinetics of the electron transfer, as evidenced by its increasing half-width. See: Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980.

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mmol) in 400 mL of dry toluene. The resulting solution was then stirred at room temperature for 4 h. After the evaporation of half of the solution, dry pentane (150 mL) was added to facilitate the precipitation of $ZnCl_2$ and the yellow solution obtained was filtered under nitrogen. After evaporation of solvents, complex **2** was obtained as a yellow powder which can be used without further purification. Yield: 5.90 g (85%).

Preparation of [RuCp*(tmpb)Cl] (3). A 300-mL flask was charged with 4.31 g (12.20 mmol) of complex **2** and 100 mL of THF. After 5 min of stirring, 3 g (12.20 mmol) of biphosphinine **1** was added and the resulting solution was heated at 35 °C for 2 h. After this period, a ^{31}P NMR control indicated the total disappearance of **1** and the formation of complex **3**. After cooling at room temperature, THF was evaporated and the red powder obtained was triturated with hexane (50 mL). The insoluble solid was then collected by filtration, washed three times with hexane (100 mL), and dried in vacuo. Complex **3** was recovered as a red-brown solid which can be crystallized at −20 °C in a THF/hexane (2:1) mixture. Yield: 5.36 g (85%).

^{31}P NMR ($CDCl_3$): δ 224.60. ^1H NMR ($CDCl_3$): δ 1.93 (t, 15H, $^4J(H-P) = 2.80$, Me of C_5Me_5), 2.39 (d, 6H, $^4J(H-P) = 4.60$, Me of tmbp), 2.46 (s, 6H, Me of tmbp), 8.12 (AA′XX′, 2H, $\Sigma J(H-P) = 17.00$, H_3 or H_6 of tmbp), 8.26 (AA′XX′, vd, 2H, $\Sigma J(H-P) = 24.00$, H_6 or H_3 of tmbp). ^{13}C NMR ($CDCl_3$): δ 11.80 (s, Me of C_5Me_5), 23.10 (s, Me of tmbp), 24.80 (AXX′, vt, $\Sigma J(C-P) = 4.30$, Me of tmbp), 94.70 (s, Cq of C_5Me_5), 130.40 (AXX′, $\Sigma J(C-P) = 41.60$, C_3 of tmbp), 132.90 (AXX′, $\Sigma J(C-P) = 38.20$, C_4 or C_5 of tmbp), 139.90 (AXX′, $\Sigma J(C-P) = 17.10$, C_6 of tmbp), 146.10 (AXX′, $\Sigma J(C-P) = 36.50$, C_4 or C_5 of tmbp), 157.05 (AXX′, vt, $\Sigma J(C-P) = 68.70$, C_2 of tmbp). Anal. Calcd for $C_{24}H_{31}ClP_2Ru$: C, 55.64; H, 6.03. Found: C, 56.39; H, 6.26.

Preparation of [RuCp*(tmpb)Br] (4). A 50 mL flask was charged with 0.1 g (0.19 mmol) of complex **3**, 5 mL of CH_2Cl_2, and 5 mL of MeOH. After complete dissolution, 0.165 g of LiBr (1.90 mmol) was added and the solution was stirred at room temperature. The metathesis was monitored by ^{31}P NMR. After 5 h, the solvents were evaporated and the brown oil obtained was partially dissolved in CH_2Cl_2 (10 mL). The resulting solution was then filtered on celite under nitrogen. The evaporation of the solvent yielded complex **4** as a brown-red solid, which was crystallized in a THF/hexane mixture (1/1). Yield: 0.085 g (80%).

^{31}P NMR ($CDCl_3$): δ 222.20. ^1H NMR ($CDCl_3$): δ 1.88 (t, 15H, $^4J(H-P) = 2.70$, Me of C_5Me_5), 2.31−2.34 (m, 12H, 4 × Me of tmbp), 7.98 (AA′XX′, vt, 2H, $\Sigma J(H-P) = 13.50$, H_3 or H_6 of tmbp), 8.36 (AA′XX′, vt, 2H, $\Sigma J(H-P) = 20.87$, H_6 or H_3 of tmbp). Anal. Calcd for $C_{24}H_{31}BrP_2Ru$: C, 51.24; H, 5.55. Found: C, 51.05; H, 5.68.

Preparation of [RuCp*(tmpb)CN] (5). A 100 mL flask was successively charged with 0.30 g (0.58 mmol) of complex **3**, 20 mL of CH_2Cl_2, and 10 mL of MeOH. After complete dissolution, 0.11 g (1.70 mmol) of KCN was added and the reaction mixture was stirred at room temperature. After 3 h a ^{31}P NMR control indicated the end of the reaction. The solvents were evaporated, and the brown residue obtained was partially dissolved in CH_2Cl_2 (40 mL). After filtration of the resulting solution on Celite under nitrogen, the CH_2Cl_2 was evaporated, yielding a brown-orange solid. After crystallization in a CH_2Cl_2/hexane mixture at −20 °C, complex **5** was isolated as a dark orange solid. Yield: 0.26 g (90%).

^{31}P NMR ($CDCl_3$): δ 220.27. ^1H NMR ($CDCl_3$): δ 2.09 (t, 15H, $^4J(H-P) = 2.42$, Me of C_5Me_5), 2.44 (d, 6H, $J(H-P) = 5.09$, Me of tmbp), 2.51 (s, 6H, Me of tmbp), 8.10 (AA′XX′, 2H, $\Sigma J(H-P) = 3.0$, H_3 or H_6 of tmbp), 8.26 (AA′XX′, s, 2H, H_6 or H_3 of tmbp). ^{13}C NMR ($CDCl_3$): δ 12.05 (s, Me of C_5Me_5), 23.15 (s, Me of tmbp), 24.94 (d, $J(C-P) = 10.50$, Me of tmbp), 97.80 (s, Cq of C_5Me_5), 128.70 (bs, C≡N), 130.91 (AXX′, $\Sigma J(C-P) = 31.70$, C_3 of tmbp), 133.64 (AXX′, $\Sigma J(C-P) = 24.30$, C_4 or C_5 of tmbp), 140.05 (AXX′, $\Sigma J(C-P) = 22.60$, C_6 of tmbp), 146.65 (AXX′, $\Sigma J(C-P) = 18.40$, C_4 or C_5 of tmbp), 152.75 (AXX′, vt, $\Sigma J(C-P) = 70.70$, C_2 of tmbp). IR (CH_2Cl_2): 2112 cm^{-1} (C≡N). Complex **5** did not give satisfactory elemental analysis data.

Preparation of [RuCp*(tmpb)(MeCN)][PF$_6$] (6). A 100 mL flask was charged with 30 mL of CH_2Cl_2, 0.24 g (1.5 mmol) of NH_4PF_6, and 2 mL of MeCN. After 5 min of stirring, 0.52 g (1 mmol) of complex **3** was added and the resulting mixture was stirred at room temperature. After 6 h, a ^{31}P NMR control indicated the end of the complexation. The CH_2Cl_2 and the excess MeCN were then evaporated, leaving a brown solid which was dissolved in CH_2Cl_2 (30 mL). The resulting solution was then filtered under nitrogen (elimination of NH_4Cl and excess of NH_4PF_6) and the solvent was removed in vacuo, yielding a yellow solid. Complex **6** was obtained as yellow microcrystals after standing in a CH_2Cl_2/ether solution at −20 °C for 1 day. Yield: 0.57 g (85%).

^{31}P NMR (CD_2Cl_2): δ 215.30 (P of tmbp), −144.40 (sept, $^1J(P-F) = 710.0$, PF_6). ^1H NMR (CD_2Cl_2): δ 1.94 (t, 15H, $J(H-P) = 2.90$, Me of C_5Me_5), 2.13 (t, 3H, $^5J(H-P) = 1.50$, Me of CH_3CN), 2.47 (d, 6H, $^4J(H-P) = 5.40$, Me of tmbp), 2.54 (s, 6H, Me of tmbp), 8.27 (AA′XX′, 2H, $\Sigma J(H-P) = 18.70$, H_3 or H_6 of tmbp), 8.38 (AA′XX′, 2H, $\Sigma J(H-P) = 24.90$, H_6 or H_3 of tmbp). ^{13}C NMR (CD_2Cl_2): δ 4.80 (s, Me of CH_3CN), 11.50 (s, Me of C_5Me_5), 23.10 (s, Me of tmbp), 24.70 (AXX′, vt, $\Sigma J(C-P) = 4.60$, Me of tmbp), 96.20 (s, Cq of C_5Me_5), 125.90 (s, CN of CH_3CN), 131.30 (AXX′, $\Sigma J(C-P) = 33.70$, C_3 of tmbp), 136.30 (AXX′, $\Sigma J(C-P) = 26.00$, C_4 or C_5 of tmbp), 141.80 (AXX′, $\Sigma J(C-P) = 20.00$, C_6 of tmbp), 148.10 (AXX′, $\Sigma J(C-P) = 26.10$, C_4 or C_5 of tmbp), 155.00 (AXX′, vt, $\Sigma J(C-P) = 35.00$, C_2 of tmbp). Anal. Calcd for $C_{26}H_{34}F_6NP_3Ru$: C, 46.70; H, 5.13. Found: C, 46.33; H, 5.36.

Preparation of [RuCp*(tmpb)(Py)][PF$_6$] (7). A 100 mL flask was charged with 30 mL of CH_2Cl_2, 0.24 g (1.5 mmol) of NH_4PF_6, and 0.30 mL (3.72 mmol) of pyridine. After 5 min of stirring, 0.52 g (1 mmol) of complex **3** was added and the resulting mixture was stirred at 40 °C. The complexation of pyridine was checked by ^{31}P NMR. After 1 h, the solvent and excess pyridine were evaporated, yielding a viscous brown resisdue which was washed three times with dry ether (20 mL). After each washing, the solution of ether was filtered off and the brown powder obtained was collected. Dry CH_2Cl_2 (20 mL) was then added, and the resulting solution was quickly filtered on Celite under nitrogen. The evaporation of CH_2Cl_2 yielded complex **7** as an orange solid which can be purified by crystallization in a CH_2Cl_2/ether mixture at −20 °C for 1 day. Yield: 0.53 g (75%).

^{31}P NMR ($CDCl_3$): δ 217.30 (P of tmbp), −145.10 (sept, $^1J(P-F) = 712.10$, PF_6). ^1H NMR ($CDCl_3$): δ 1.81 (t, 15H, $^4J(H-P) = 2.80$, Me of C_5Me_5), 2.44 (d, 6H, $J(H-P) = 5.10$, Me of tmbp), 2.58 (s, 6H, Me of tmbp), 7.20 (dd, 2H, $^3J(H-H) = 5.10$ and 7.90, $H_{3,5}$ of C_5H_5N), 7.57 (t, 1H, $^3J(H-H) = 7.90$, H_4 of C_5H_5N), 8.15 (AA′XX′, 2H, $\Sigma J(H-P) = 18.20$, H_3 or H_6 of tmbp), 8.55 (d, 2H, $^3J(H-H) = 5.10$, $H_{2,6}$ of C_5H_5N), 8.56 (AA′XX′, 2H, $\Sigma J(H-P) = 24.80$, H_6 or H_3 of tmbp). ^{13}C NMR (CD_2Cl_2): δ 11.30 (s, Me of C_5Me_5), 23.00 (s, Me of tmbp), 24.70 (AXX′, vt, $J(C-P) = 4.50$, Me of tmbp), 95.80 (s, Cq of C_5Me_5), 126.70 (s, C_3 of C_5H_5N), 131.20 (AXX′, $\Sigma J(C-P) = 33.90$, C_3 of tmbp), 136.20 (AXX′, $\Sigma J(C-P) = 30.50$, C_4 or C_5 of tmbp), 138.50 (s, C_4 of C_5H_5N), 141.20 (AXX′, $\Sigma J(C-P) = 39.70$, C_6 of tmbp), 148.40 (AXX′, $\Sigma J(C-P) = 25.80$, C_4 or C_5 of tmbp), 154.90 (AXX′, vt, $\Sigma J(C-P) = 70.30$, C_2 of tmbp), 158.80 (t, $^3J(C-P) = 4.80$, C_2 of C_5H_5N). Anal. Calcd for $C_{29}H_{36}F_6NP_3Ru$: C, 49.29; H, 5.13. Found: C, 49.57; H, 4.89.

Preparation of [RuCp*(tmpb)(P(OMe)$_3$)][PF$_6$] (8). A 100 mL flask was charged with 30 mL of CH_2Cl_2, 0.24 g (1.5 mmol) of NH_4PF_6, and 0.25 mL of trimethyl phosphite. After 5 min of stirring, 0.52 g (1 mmol) of complex **3** was added and the resulting mixture was stirred at room temperature. After 2 h, a ^{31}P NMR control indicated the quantitative transformation of **3** into complex **8**. The solvent was then evaporated, and the resulting brown residue was triturated with dry ether (20 mL). After filtration of the ether phase, the brown powder obtained was dissolved in CH_2Cl_2 (30 mL) and then filtered

on Celite under nitrogen. After evaporation of CH_2Cl_2, complex **8** was obtained as a yellow powder (0.66 g) which was crystallized in a CH_2Cl_2/ether (1:1) mixture at −20 °C for 1 day. Complex **8** was then collected as yellow microcrystals after filtration and drying. Yield: 0.60 g (80%).

^{31}P NMR ($CDCl_3$): δ 217.90 (d, $^2J(P-P) = 72.10$, P of tmbp), 144.40 (t, $^2J(P-P) = 72.10$, P of $P(OMe)_3$), −146.15 (sept, $^1J(P-F) = 713.85$, PF_6). ^1H NMR ($CDCl_3$): δ 2.05 (t, 15H, $^4J(H-P) = 2.50$, Me of C_5Me_5), 2.48 (d, 6H, $J(H-P) = 5.50$, Me of tmbp), 2.57 (s, 6H, Me of tmbp), 3.37 (d, 9H, $^3J(H-P) = 12.20$, Me of $P(OMe)_3$), 8.24 (AA′XX′, 2H, $\Sigma J(H-P) = 18.50$, H_3 or H_6 of tmbp), 8.35 (AA′XX′, 2H, $\Sigma J(H-P) = 20.90$, H_6 or H_3 of tmbp). ^{13}C NMR (CD_2Cl_2): δ 11.40 (s, Me of C_5Me_5), 23.00 (s, Me of tmbp), 24.80 (d, $J(C-P) = 6.20$, Me of tmbp), 53.40 (s, Me of $P(OMe)_3$), 99.70 (s, Cq of C_5Me_5), 131.80 (AXX′, $\Sigma J(C-P) = 31.60$, C_3 of tmbp), 136.00 (AXX′, $\Sigma J(C-P) = 25.80$, C_4 or C_5 of tmbp), 141.30 (AXX′, $\Sigma J(C-P) = 29.80$, C_6 of tmbp), 148.50 (AXX′, $\Sigma J(C-P) = 18.30$, C_4 or C_5 of tmbp), 153.30 (AXX′, vt, $\Sigma J(C-P) = 75.30$, C_2 of tmbp). Anal. Calcd for $C_{27}H_{40}F_6O_3P_4Ru$: C, 43.14; H, 5.36. Found: C, 43.21; H, 5.35.

Preparation of [RuCp*(tmpb)(PPh_3)][PF_6] (9). A 100 mL flask was charged with 30 mL of CH_2Cl_2, 0.24 g (1.5 mmol) of NH_4PF_6, and 0.40 g (1.50 mmol) of triphenylphosphine. After 5 min of stirring, 0.52 g (1 mmol) of complex **3** was added and the resulting mixture was stirred at room temperature. After 10 h, a ^{31}P NMR control indicated the quantitative transformation of **3** into complex **9**. After CH_2Cl_2 (20 mL) was added, the solution was filtered under nitrogen and the solvent was partially evaporated. Ether (30 mL) was then added to the resulting solution (about 5 mL) to precipitate complex **9**. After filtration of the ether phase, **9** was partially dried under vacuum and then washed with dry hexane (40 mL). After elimination of hexane by filtration, the complex was recovered as a yellow powder. Long yellow needles of **9** were isolated after a crystallization with CH_2Cl_2/ether (1:1). Yield: 0.71 g (80%).

^{31}P NMR ($CDCl_3$): δ 226.20 (d, $^2J(P-P) = 51.65$, P of tmbp), 46.95 (t, $^2J(P-P) = 51.65$, P of PPh_3), −143.96 (sept, $^1J(P-F) = 713.85$, PF_6). ^1H NMR ($CDCl_3$): δ 1.76 (t, 15H, $^4J(H-P) = 2.50$, Me of C_5Me_5), 2.35 (d, 6H, $J(H-P) = 5.70$, Me of tmbp), 2.55 (s, 6H, Me of tmbp), 7.10−7.32 (m, 15H, C_6H_5), 7.79 (AA′XX′, 2H, $\Sigma J(H-P) = 20.57$, H_3 or H_6 of tmbp), 8.34 (AA′XX′, 2H, $\Sigma J(H-P) = 22.97$, H_6 or H_3 of tmbp). ^{13}C NMR (CD_2Cl_2): δ 11.65 (s, Me of C_5Me_5), 23.10 (s, Me of tmbp), 25.10 (AXX′, $\Sigma J(C-P) = 11.0$, Me of tmbp), 98.80 (s, Cq of C_5Me_5), 128.50−135.0 (m, C_6H_5 and 2 carbons of tmbp (C_3 and C_4 or C_5)), 140.24 (AXX′, $\Sigma J(C-P) = 27.75$, C_6 of tmbp), 148.25 (AXX′, $\Sigma J(C-P) = 20.20$, C_4 or C_5 of tmbp), 153.20 (AXX′, vt, $\Sigma J(C-P) = 76.20$, C_2 of tmbp). Anal. Calcd for $C_{42}H_{46}F_6P_4Ru$: C, 56.69; H, 5.21. Found: C, 56.80; H, 5.50.

Preparation of [RuCp*(tmpb)(C_7H_8BrP)][PF_6] (10). A 100 mL flask was charged with 30 mL of CH_2Cl_2, 3 mL of methanol, 0.24 g (1.5 mmol) of NH_4PF_6, and 0.22 g (1.1 mmol) of 2-bromo-4,5-dimethylphosphinine. After 5 min of stirring, 0.52 g (1 mmol) of complex **3** was added and the resulting mixture was stirred at room temperature. After 4 h, a ^{31}P NMR control indicated the end of the reaction. The resulting reaction mixture was then evaporated to dryness and the brown viscous residue obtained was triturated and washed three times with hexane (3 × 30 mL). The hexane phase which contains excess 2-bromophosphinine was separated from the solid by filtration under nitrogen. After drying, dry CH_2Cl_2 (20 mL) was added and the resulting solution was filtered on Celite under nitrogen. Complex **10** was recovered as a yellow powder after evaporation of CH_2Cl_2. Yield: 0.70 g (85%).

^{31}P NMR ($CDCl_3$): δ 208.80 (d, $^2J(P-P) = 66.80$, P of tmbp), 184.40 (t, $^2J(P-P) = 66.80$, P of C_7H_8PBr), −146.15 (sept, $^1J(P-F) = 713.85$, PF_6). ^1H NMR ($CDCl_3$): δ 2.08 (d, 15H, $^4J(H-P) = 2.50$, Me of C_5Me_5), 2.17 (d, 3H, $J(H-P) = 6.40$, Me of C_7H_8PBr), 2.23 (s, 3H, Me of C_7H_8PBr), 2.45 (d, 6H, $J(H-P) = 5.50$, Me of tmbp), 2.59 (s, 6H, Me of tmbp), 7.81 (m, 2H, $\Sigma J(H-P) = 30.40$, H of C_7H_8PBr), 8.24 (AA′XX′, 2H, $\Sigma J(H-P) = 20.70$, H_3 or H_6 of tmbp), 8.59 (AA′XX′, 2H, $\Sigma J(H-P) = 22.70$, H_6 or H_3 of tmbp). ^{13}C NMR ($CDCl_3$): δ 12.10 (s, Me of C_5Me_5), 22.20 (d, $J(C-P) = 3.50$, Me of C_7H_8PBr), 23.20 (d, $J(C-P) = 3.90$, Me of tmbp), 23.70 (d, $J(C-P) = 10.70$, Me of C_7H_8PBr), 25.10 (d, $J(C-P) = 10.90$, Me of tmbp), 99.80 (s, Cq of C_5Me_5), 131.60 (AXX′, $\Sigma J(C-P) = 30.40$, C_3 of tmbp), 136.40 (AXX′, $\Sigma J(C-P) = 25.70$, C_4 or C_5 of tmbp), 139.10 (d, $J(C-P) = 24.50$, C_2 of C_7H_8PBr), 142.90 (AXX′, $\Sigma J(C-P) = 28.20$, C_6 of tmbp), 144.40 (m, $\Sigma J(C-P) = 11.20$, C_3 of C_7H_8PBr), 148.70 (AXX′, $\Sigma J(C-P) = 18.50$, C_4 or C_5 of tmbp), 148.80 (m, $\Sigma J(C-P) = 22.80$, C_4 or C_5 of C_7H_8PBr), 152.60 (AXX′, $\Sigma J(C-P) = 23.20$, C_6 of C_7H_8PBr), 153.30 (AXX′, vt, $\Sigma J(C-P) = 74.10$, C_2 of tmbp). Anal. Calcd for $C_{31}H_{39}BrF_6P_4Ru$: C, 44.83; H, 4.73. Found: C, 44.55; H, 5.13.

Preparation of [RuCp*(tmpb)(CNtBu)][PF_6] (11). A 100 mL flask was charged with 30 mL of CH_2Cl_2, 0.24 g (1.5 mmol) of NH_4PF_6, and 0.52 g (1 mmol) of complex **3**. After 5 min of stirring, 0.25 mL (1.92 mmol) of *tert*-butyl isocyanide was added and the reaction mixture was stirred at room temperature. After 30 min a control by ^{31}P NMR indicated the end of the reaction with quantitative formation of complex **11**. The solvent was then evaporated, yielding an orange viscous oil which was triturated and washed three times with dry ether (20 mL). After each washing, the ether phase was separated from the solid by filtration. Complex **11** was then extracted with CH_2Cl_2 (30 mL) and filtered on Celite under nitrogen. The evaporation of CH_2Cl_2 yielded **11** as a dark green solid which can be crystallized in a CH_2Cl_2/ether (1:1) mixture at −20 °C. Yield: 0.46 g (65%).

^{31}P NMR ($CDCl_3$): δ 210.90 (P of tmbp), −146.05 (sept, $^1J(P-F) = 711.65$, PF_6). ^1H NMR ($CDCl_3$): δ 1.25 (s, 9H, Me of $C(CH_3)_3$), 2.09 (t, 15H, $^4J(H-P) = 2.80$, Me of C_5Me_5), 2.50 (d, 6H, $J(H-P) = 5.70$, Me of tmbp), 2.57 (s, 6H, Me of tmbp), 8.31 (AA′XX′, 2H, $\Sigma J(H-P) = 20.20$, H_3 or H_6 of tmbp), 8.34 (AA′XX′, 2H, $\Sigma J(H-P) = 23.40$, H_6 or H_3 of tmbp). ^{13}C NMR ($CDCl_3$): δ 11.70 (s, Me of C_5Me_5), 23.20 (s, Me of tmbp), 24.90 (d, $J(C-P) = 10.70$, Me of tmbp), 31.30 (s, Me of $C(CH_3)_3$), 58.70 (s, Cq of $C(CH_3)_3$), 99.20 (s, Cq of C_5Me_5), 131.70 (AXX′, $\Sigma J(C-P) = 30.60$, C_3 of tmbp), 136.20 (AXX′, $\Sigma J(C-P) = 25.60$, C_4 or C_5 of tmbp), 141.50 (AXX′, $\Sigma J(C-P) = 24.70$, C_6 of tmbp), 148.30 (AXX′, $\Sigma J(C-P) = 22.10$, C_4 or C_5 of tmbp), 153.60 (AXX′, vt, $\Sigma J(C-P) = 71.90$, C_2 of tmbp). IR (CCl_4): 2143 cm^{-1} (C≡N). Anal. Calcd for $C_{29}H_{40}F_6NP_3Ru$: C, 49.01; H, 5.67. Found: C, 48.67; H, 5.78.

Preparation of [RuCp*(tmpb)(η^2-*cis*-C_8H_{14})][PF_6] (12). A 100 mL flask was charged with 30 mL of CH_2Cl_2, 0.24 g (1.5 mmol) of NH_4PF_6, and 0.52 g (1 mmol) of complex **3**. After 5 min of stirring, 1 mL (7.68 mmol) of *cis*-cyclooctene was added and the reaction mixture was stirred at room temperature. After 2 h, a control by ^{31}P NMR indicated the end of the complexation. The reaction mixture was then evaporated to dryness, yielding a green powder which was washed three times with dry hexane (20 mL) to remove traces of cyclooctene. After each washing, the hexane phase was separated from the solid by filtration under nitrogen. The resulting residue was then dissolved in dry CH_2Cl_2 (20 mL) and filtered on Celite under nitrogen. After evaporation of CH_2Cl_2, complex **12** was recovered as a dark green powder which can be crystallized in a CH_2Cl_2/ether (1:1) mixture at room temperature. Yield: 0.37 g (50%).

^{31}P NMR (CD_2Cl_2): δ 232.70 (P of tmbp), −143.25 (sevt, $^1J(P-F) = 712.85$, PF_6). ^1H NMR (CD_2Cl_2): δ 1.2−1.5 (m, 12H, CH_2 of C_8H_{14}), 1.76 (t, 15H, $^4J(H-P) = 2.70$, Me of C_5Me_5), 2.42 (d, 6H, $J(H-P) = 5.00$, Me of tmbp), 2.50 (s, 6H, Me of tmbp), 3.04 (d, 2H, $^3J(H-H) = 10.10$, CH of C_8H_{14}), 8.21 (AA′XX′, m, 4H, H_3 and H_6 of tmbp). ^{13}C NMR (CD_2Cl_2): δ 10.80 (s, Me of C_5Me_5), 23.30 (s, Me of tmbp), 25.20 (AXX′, vt, $\Sigma J(C-P) = 5.40$, Me of tmbp), 26.40, 32.80, 33.50 (s, CH_2 of C_8H_{14}), 74.80 (s, =CH of C_8H_{14}), 99.00 (s, Cq of C_5Me_5), 131.40 (AXX′, $\Sigma J(C-P) = 48.10$, C_3 of tmbp), 136.60 (AXX′, $\Sigma J(C-P) = 23.30$, C_4 or C_5 of tmbp), 140.20 (AXX′, $\Sigma J(C-P) = 26.50$, C_6 of tmbp), 149.10 (AXX′, $\Sigma J(C-P) = 13.90$, C_4 or C_5 of tmbp),

152.00 (AXX′, vt, ΣJ(C−P) = 76.30, C_2 of tmbp). Complex **12** did not give satisfactory elemental analysis data.

Preparation of [RuCp*(tmpb)(η^2-C_7H_{10})][PF_6] (13). The experimental procedure is identical with that used for the preparation of complex **12**. The reaction occurs under the same conditions and requires 2 h of stirring at room temperature. From 0.24 g (1.5 mmol) of NH_4PF_6, 0.52 g (1 mmol) of complex **3**, and 0.19 g (2 mmol) of norbornene, complex **13** was isolated as a dark green solid after crystallization in a CH_2Cl_2/ether mixture (1:1) at −20 °C. Yield: 0.50 g (70%).

^{31}P NMR (CD_2Cl_2): δ 234.90 (P of tmbp), −144.35 (sept, ^1J(P−F) = 708.70, PF_6). ^{1}H NMR (CD_2Cl_2): δ 1.03−2.30 (m, 23H, Me of C_5Me_5, 2 × CH and 2 × CH_2 of C_7H_{10}), 2.48 (d, 6H, J(H−P) = 4.90, Me of tmbp), 2.57 (bs, 6H, Me of tmbp), 2.97 (bs, 2H, CH of C_7H_{10}), 8.28 (AA′XX′, 2H, ΣJ(H−P) = 16.70, H_2 or H_6 of tmbp), 8.40 (AA′XX′, 2H, ΣJ(H−P) = 19.50, H_6 or H_2 of tmbp). ^{13}C NMR (CD_2Cl_2): δ 10.15 (s, Me of C_5Me_5), 22.60 (s, Me of tmbp), 24.55 (s, Me of tmbp), 27.85 (s, CH_2 of C_7H_{10}), 35.0 (s, CH of C_7H_{10}), 42.35 (s, bridging CH_2 of C_7H_{10}), 67.95 (s, =CH of C_7H_{10}), 99.55 (Cq of C_5Me_5), 131.85 (AXX′, ΣJ(C−P) = 48.82, C_3 of tmbp), 136.45 (AXX′, C_4 or C_5 of tmbp), 140.10 (AXX′, ΣJ(C−P) = 27.46, C_6), 148.55 (AXX′, ΣJ(C−P) = 37.80, C_5 or C_4), 151.20 (AXX′, vt, ΣJ(C−P) = 76.30, C_2); Anal. Calcd for $C_{31}H_{41}F_6P_3Ru$: C, 51.59; H, 5.73. Found: C, 51.38; H, 5.85.

Electrochemical Study of 3. Transient cyclic voltammetry was performed in a ca. 12 mL three-electrode airtight cell connected to a Schlenk line. The working electrode consisted of a gold disk of 0.5 or 0.125 mm diameter made from a cross section of a gold wire (Goodfellow) sealed in glass. The reference electrode was an SCE (Tacussel), separated from the solution by a bridge (3 mL) filled with a 0.3 M solution of *n*-Bu_4NBF_4 in MeCN identical with that used in the cell. The counter electrode was a platinum spiral of ca. 1 cm^2 apparent surface located within 5 mm of the working electrode and facing it. A home-built potentiostat equipped with positive feedback for ohmic-drop compensation[19] was used. The potential wave form signal generator was a Tacusssel GSTP4 instrument. The voltammograms were recorded with a Nicolet 3091 digital oscilloscope and the measurements performed on the stored curves. The cyclic voltammetric measurements were performed on 2 mM solutions of the complex. The absolute number of electrons was determined by a combination of chronoamperometry and cyclic voltammetry on a stationary gold-disk ultramicroelectrode (0.25 μm), with ferrocene as reference, according to a published procedure.[16]

X-ray Structure Determination for 3. Crystals of **3**, $C_{28}H_{39}ClOP_2Ru$, were grown from a THF/pentane solution of the compound. Data were collected at −150 ± 0.5 °C on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation (λ = 0.710 73 Å) and a graphite monochromator. The crystal structure was solved and refined using the Enraf-Nonius MOLEN package. The compound crystallizes in space group $P2_1/n$ (No. 14), with a = 11.493(1) Å, b = 14.238(1) Å, c = 16.605(2) Å, β = 92.56(6)°, V = 2714.52(77) Å^3, Z = 4, d_{calc} = 1.444 g/cm^3, μ = 8.0 cm^{-1}, and F(000) = 1224. A total of 8561 unique reflections were recorded in the range $2° \le 2\theta \le 60.0°$, 2916 of which were considered as unobserved ($F^2 < 3.0\sigma(F^2)$), leaving 5644 for solution and refinement. Direct methods yielded a solution for most atoms. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. A non-Poisson weighting scheme was applied with a p factor equal to 0.08. The final agreement factors were R = 0.038, R_w = 0.060, and GOF = 1.20.

Supporting Information Available: Text giving details of the X-ray structure determination for **3** and tables of crystal data, positional parameters, bond distances and angles for all non-hydrogen atoms, and β_{ij} values (6 pages). Ordering information is given on any current masthead page.

OM960063J

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