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NHC-Derived Bis(amidiniophosphine) Ligands of Rh(I) Complexes: Versatile cis−trans Chelation Driven by an Interplay of Electrostatic and Orbital Effects§

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The synthesis, structure, and electronic properties of a dicationic bis(amidiniophosphine) based on an *o*-phenylene bridge is described. In spite of the presence of two facing P-conjugated positive charges, this electron-poor diphosphine is shown to act as a versatile chelating ligand in a series of stable rhodium(I) complexes. IR analysis of a carbonyl complex showed that the σ-donating versus π-accepting character of the cationic ligand is comparable to that of a neutral trialkylphosphite. While the ligand is trans-chelating at a neutral Rh(I) center, it switches to cis-chelating at a cationic Rh^+ center. This and other unusual geometrical features revealed by X-ray diffraction analyses are interpreted by a subtle interplay between antisymbiotic trans preference, electrostatic repulsion, and relative Lewis acidity of the transition metal centers.

Introduction

After the discovery of the Wilkinson complexes[1] and decades of variation of the structure of phosphane ligands, all basic possibilities for tuning their steric and donor/acceptor characters seemed to have been explored, but the emergence of the so-called N-heterocyclic carbenes (NHCs) opened new horizons in catalysis.[2] Today and more than ever, the design of a novel category of phosphane ligands might thus be regarded as a wager. Nevertheless, since direct anchoring of NHCs to metals provided *complexes* with unprecendented properties, anchoring of NHCs to P(III) atoms was likely to provide *ligands* with unprecendented properties as well. Following early reports by Komarov et al.[3] and Kuhn et al.,[4] complexes of NHC−P(III) ligands thus deserved more systematic attention, which was paid in a few recent reports.[5,6] Although both theoretical calculations[7] and X-ray diffraction analyses[6] suggested that these ligands could indeed be described as NHC−phosphenium adducts, in the absence of definite experimental evidence (e.g., through examples of selective displacement of the NHC "ligand" by weak nucleophiles), the free molecules are basically represented as amidiniophosphanes, where the cationic charge is located at an sp^2 nitrogen atom. This Lewis picture simply illustrates the possibility of complexation of the neutral P(III) center to electropositive transition metal centers. Nevertheless, the NHC−phosphenium picture also accounts for the coordinating ability by a simple orbital comparison with NHC−metal complexes: whereas the latter present electron-rich metal centers favoring oxidative addition of C−X bonds, NHC−phospheniums should present sufficiently electron-rich P(III) centers favoring complexation to Lewis acidic transition metals (Scheme 1).

Whatever the picture is, however, the cationic charge is conjugated to the P(III) center, and amidiniophosphanes are expected to be weakly σ-donating ligands. In marked contrast to the electron-rich ligands (NHCs and others), which were extensively investigated for their catalytic properties

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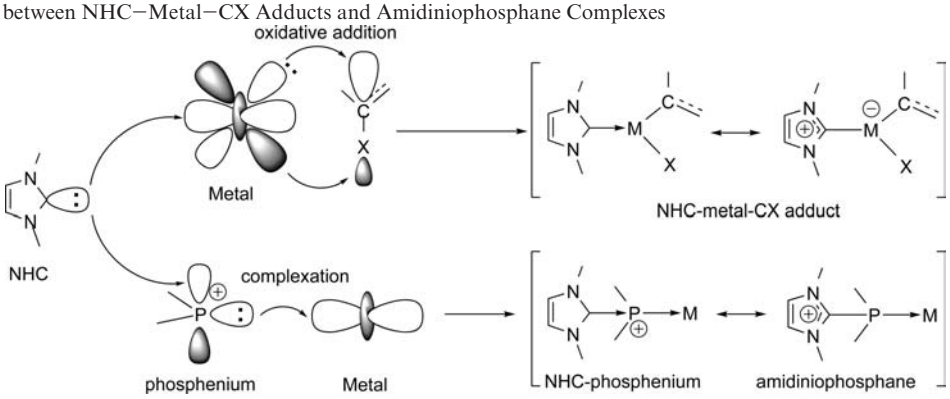
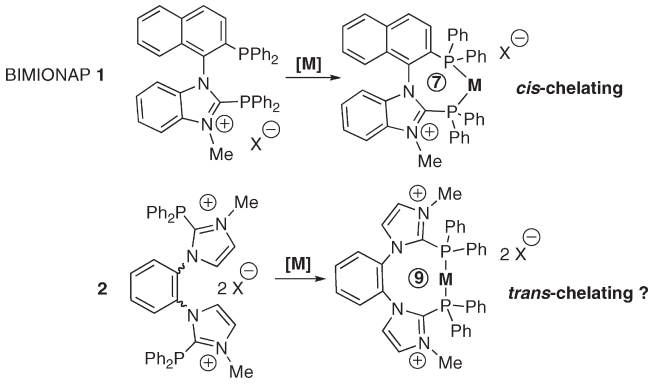
Scheme 1. Analogy between NHC−Metal−CX Adducts and Amidiniophosphane Complexes



(Scheme 1),[2] the electron-poor ligands remained less explored. Few catalytic processes were, however, shown to benefit from the use of electron-deficient ligands,[8] in particular when the Lewis acidity of the metallic center was crucial.[9] Paradigms of electron-poor ligands are phosphites, the electron-withdrawing effects of which result from both σ-(−I)-induction and π-retrodonation into the π^* orbitals of the P−O linkages.[10] Since P−O bonds are, however, sensitive to protic cleavage, fluoroarylphosphines, with inert P−C bonds, were also considered as alternatives.[11] Their structural diversity is however limited, and the apparent robustness of the amidiniophosphanes makes them attractive candidates for mimicking the electron deficiency of phosphites, while providing an essential difference: the conjugation of a cationic charge with the coordinating P(III) atom. Cationic phosphanes bearing quaternary ammonium[12] or phosphonium[13] moieties have long been investigated for the design of "true" zwitterionic organometallates[14] or for performing catalysis in aqueous media.[15] In most cases, however, their positive charge was conjugatively isolated in remote position from the P(III) atom in order to avoid perturbation of the metal center. The "vicinal electrostatics" are thus a fundamental feature of the amidiniophosphane ligands.

Scheme 2. Comparison between the Possible Coordination Modes of the Monocationic BIMIONAP Ligand **1** and the Targeted Dicationic Ligand **2**



Beyond their *monodentate* versions,[3−5] amidiniophosphane ligands were recently exemplified in the *chelate* version by a palladium(II) complex of the BIMIONAP ligand **1**, combining a cationic amidiniophosphine end with a neutral phosphine end.[6] Considering the "optimal" selectivity of C_2-symmetric chelating ligands in catalysis, the next challenge was therefore the design of bis(amidiniophosphane) ligands, where the electrostatics are expected to become critical: the repulsion between the two cationic charges should indeed be destabilizing. Taking this constraint into consideration, ligand **2** was devised as a suitable candidate, where the *o*-phenylene bridge between the two charges is expected to act as an insulating rigid link (Scheme 2). Whereas BIMIONAP **1** was shown to act as a cis-chelating ligand in a seven-membered metallacycle,[6] ligand **2** should afford more flexible nine-membered metallacycles, allowing the formal positive charges to repel each other in a trans coordination mode. Although the intrinsic stability of the targeted complexes is the main question, the possibility of a nonclassical trans-chelating geometry could also meet independent concerns in the coordination chemistry of diphosphane ligands.[16]

Results and Discussion

The preparation of **2** started from the readily available 1,2-bis(N-imidazolyl)benzene **3**.[17] Double deprotonation of

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3 with 2 equiv of *n*-BuLi in THF followed by addition of a stoichiometric amount of chlorodiphenylphosphine afforded the diphosphane **4** in 54% yield. A total of 2 equiv of methyl triflate (MeOTf) were then selectively reacted with **4** in CH_2Cl_2 to give the desired dication as a 7:3 mixture of isomers **2a** and **2b** in 94% yield. The ionic structure of **2** was first revealed by its low solubility in nonpolar solvents. This was confirmed by the NMR deshielding of the two equivalent ^{31}P nuclei from $\delta = -30.5$ ppm in **4** to $\delta = -21.5$ and -20.6 ppm in **2a** and **2b**, respectively. By contrast, the ^1H NMR spectrum of the **2a**/**2b** mixture displayed a single signal at $\delta = +3.41$ ppm for the N−CH_3 groups (Scheme 3).

The observation of two types of NMR signals for **2** could be tentatively attributed to the existence of two resolved conformations, and variable-temperature NMR experiments indeed revealed dynamic behavior by a reversible coalescence of the ^{31}P NMR signals of **2a** and **2b** in CD_3CN at +70 °C, corresponding to an activation barrier of ca. 16 kcal/mol. No NMR differentiation was observed for the neutral ligand **4** at room temperature, but decoalescence of its ^{31}P NMR signal in $CDCl_3$ was observed at a lower temperature (−10 °C) corresponding to an interconversion barrier between isomers **4a** and **4b** of ca. 12 kcal/mol (Scheme 3). The occurrence of isomers **2a** and **2b** at room temperature was thus ascribed to a restriction of the rotation about the N(imidazolyl)−C(aryl) bond, enhanced by electrostatic and steric repulsion between the amidiniophosphine groups. Both repulsive components are indeed absent in the neutral version **4**. Finally, the atropisomers of **2** and **4** could be interpreted by more or less locked syn/anti arrangements of the PPh_2 (respectively NMe) moieties with respect to the orthogonal *o*-phenylene mean plane (i.e., with pseudo-C_s/pseudo-C_2 symmetries).

Before their coordinating properties were studied, the electronic properties of the "free ligands" **4** and **2** were investigated by cyclic voltammetry. It was indeed shown that the oxidation potential of related symmetrical diphosphanes is an accurate measure of the electronic endowment of the PPh_2 groups.[18] The cyclic voltammograms of **2** and **4** (0.1 V s^{-1}) exhibited an irreversible single oxidation peak for the two equivalent PPh_2 groups. The values of E_p^{ox} (**4**, +1.37 V and **2**, +2.39 V vs saturated calomel electrode (SCE)) confirmed the overall electron deficiency of the dicationic species **2** with respect to its neutral analogue **4**. Moreover, the observed large difference ($\approx$ 1 V) suggested that the unconventional dicationic diphosphine **2** should indeed possess "extreme" electronic properties, at least with respect to the more conventional neutral diphosphine **4**.

The dicationic diphosphine **2** was then reacted with 0.5 equiv of $[RhCl(cod)]_2$ in CH_2Cl_2 (cod = 1,5-cyclooctadiene). The ^{31}P NMR spectrum of the reaction mixture showed the complete disappearance of the signals of **2a** and **2b** and the appearance of a main resonance at a low field (d, $\delta = +33.4$ ppm, $J_{PRh} = 153.9$ Hz). This change was attributed to the formation of complex **5**, where, despite the presence of two proximal positive charges, the diphosphine

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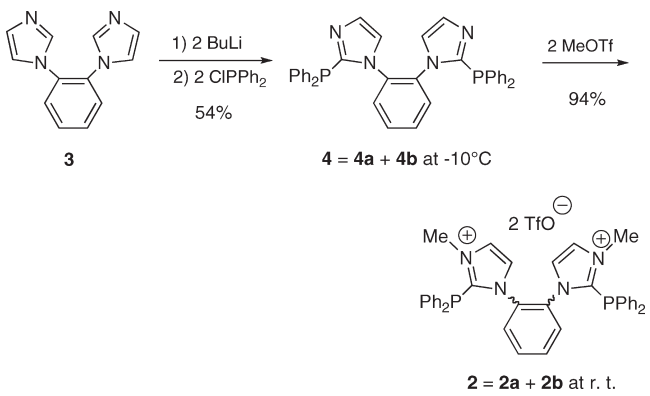
Scheme 3. Selective Phosphanylation and Methylation of 1,2-Bis (N-imidazolyl)benzene **3**



2 retains some donor character toward a moderately Lewis acidic Rh(I) center (Scheme 4). The ^{31}P NMR spectrum of the mixture was actually more complex, displaying six additional small broad doublets (Σintensity $\approx$ 30%) nearby the signal of **5** (ca. 70%), with similar J_{RhP} coupling constants. A variable-temperature NMR experiment indicated a reversible coalescence of all of the signals at +55 °C, thus demonstrating dynamic behavior and allowing assignment of the signals observed at 20 °C to seven isomers of **5**.[19]

Complex **5** proved to be sensitive and escaped many attempts at crystallization, likely because of the coexistence of an important number of isomers at room temperature. In order to analyze the coordination of **2** in terms of σ-donation versus π-back-donation and to possibly minimize the number of isomers, substitution of the cod ligand by carbonyl probes was envisaged. Following a classical procedure, a solution of **5** in CH_2Cl_2 was thus treated with an excess of CO. Rather unexpectedly, ^{31}P NMR monitoring indicated the conversion of all of the resonances of **5** to a unique resonance at $\delta = +31.3$ ppm (d, $J_{PRh} = 133.7$ Hz). This signal was assigned to complex **6**, which was finally isolated in 72% overall yield from **2**, and fully characterized. The presence of a single type of CO ligand in **6** was confirmed by the corresponding ^{13}C NMR multiplet at $\delta = +185.1$ ppm (td, $J_{CRh} = 74.2$, $J_{CP} = 15.3$ Hz), while the uniqueness of this ligand was suggested by a single IR stretching frequency at 2007 cm^{-1} (Scheme 4). If no accidental IR degeneracy occurred, the coordination mode of **2** in **6** should thus be trans-chelating.

The structure of **6** was finally confirmed by X-ray diffraction analysis of yellow crystals deposited from a MeCN/Et_2O mixture (Figure 1).[20] The Rh(I) atom is located at the center of a quasi-square-planar environment ($\Sigma° = 358.96°$), where the trans-chelating character of **2** is confirmed by the P−Rh−P and CO−Rh−Cl angles of 163.8° and 175.5°, respectively. This peculiar coordination mode of two

(19) Since ^1H and ^{13}C NMR analyses confirmed the presence of a 1, 5-cyclooctadiene (cod) ligand, **5** can be described as an 18-electron rhodium(I) complex. The triangular bipyramidal geometry consistent with such a Rh(I) center, the possible atropo-stereogenic element of the phenylene bridge, the cis/trans arrangement of the chelating diphosphine **2**, or the partial decoordination of the cod ligand might account for the existence of the stereoisomers observed at room temperature.

(20) CCDC-720873 (**6**) and CCDC-720874 (**7b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

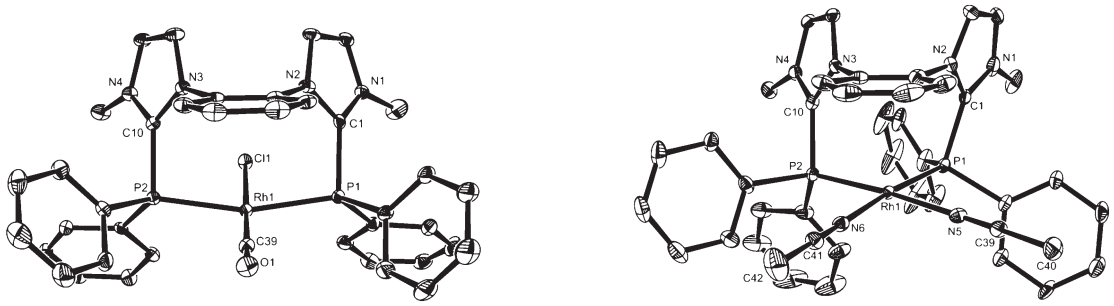
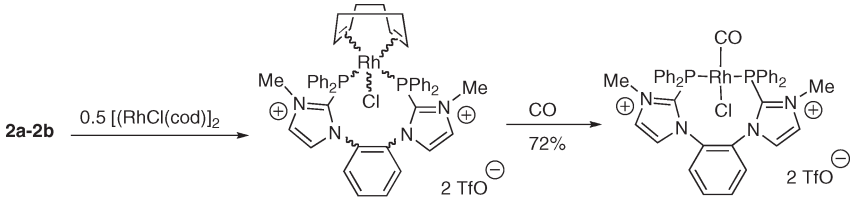


Figure 1. ORTEP views of the X-ray crystal structures of complexes **6** (left) and **7b** (right), with thermal ellipsoids drawn at the 30% probability level. Selected bond distances (Å) and angles (deg). Complex **6**: C1−P1 1.838(7), C10−P2 1.835(6), P1−Rh1 2.2721(18), P2−Rh1 2.2814(17), Cl1−Rh1 2.3646 (16), C39−Rh1 1.809(7), P2−Rh1−P1 163.77(6), Cl1−Rh1−C39 175.5(2). Complex **7b**: C1−P1 1.832(7), C10−P2 1.842(7), P1−Rh1 2.2348(17), P2−Rh1 2.2329(16), N5−Rh1 2.055(5), N6−Rh1 2.052(6), P1−Rh1−N6 173.38(16), P2−Rh1−N5 174.81(17).

Scheme 4. Preparation of Dicationic Rhodium Complexes of the Bis(amidiniophosphine) Ligand **2**



PPh_2 moieties at a *trans*-RhCl(CO) center[21] was previously observed in the corresponding monodentate amidiniophosphine series.[5b] In complex **6**, it is allowed by the size of the rhodacycle (nine-membered) and at least partly dictated by the electrostatic repulsion between the two cationic charges.

It is noteworthy that the value of the CO IR stretching frequency (2007 cm^{-1}) of **6** is on the same order of magnitude as those reported in the analogous *trans*-RhCl(CO)$[P(OMe)_3]_2$ complex (2011 cm^{-1}): the σ-donor versus π-acceptor character of the bis(amidiniophosphine) ligand **2** is therefore comparable to that of a phosphite ligand.[22] The presence of a single CO ligand can be explained by a competition between its strong π-accepting character and the electron-poor character of **2**: two CO ligands could not accommodate the electron deficiency of the Rh^+ center, which would have resulted from the displacement of the Cl^- ligand of **6**.

In order to force the abstraction of the Cl^- ligand, complex **6** was treated with a stoichiometric amount of a silver salt (AgOTf or $AgPF_6$) in MeCN at room temperature. A white precipate of AgCl deposited, while ^{31}P NMR analysis showed the formation of a new complex, **7a** (X = TfO, δ = +35.6 ppm, J_{PRh} = 178.2 Hz) or **7b** (X = PF_6, δ = +35.7 ppm, J_{PRh} = 178.3 Hz). The latter were finally isolated in 89% and 91% yield, respectively, and fully characterized (Scheme 5).

The ^{31}P chemical shifts of **7a** and **7b** are very similar to those of **6** (δ = +31.3 ppm, J_{PRh} = 133.7 Hz), but the difference in the J_{RhP} values suggested a marked geometrical change at the rhodium center. The displacement of CO and Cl^- ligands of **6** was confirmed by ^{13}C NMR and IR and by MS spectroscopy, respectively.

The exact structure was finally determined by X-ray diffraction analysis of orange single crystals of **7b** (X = PF_6) deposited from a $MeCN/Et_2O$ mixture (Scheme 5, Figure 1).[20] As in **6**, the Rh(I) atom is still located at the center of a square-planar environment ($\Sigma°$ = 359.94°), but in contrast to **6**, ligand **2** here acts in a cis-chelating manner (P−Rh−P = 96.8°). The absence of the CO ligand and the equivalence of the ^{31}P nuclei observed in solution are here explained by the cis-coordination of two MeCN molecules, endowing the cationic Rh^+ center with a 16-electron count in the globally tricationic complex **7b**.

These unanticipated results can be interpreted by the inability of the tricationic $Rh(\mathbf{2})^+$ center (resulting from the chloride abstraction) to retain the highly π-accepting CO ligand,[23] which is thus instantly expelled from the coordination sphere and replaced by MeCN molecules.

The change in the coordination mode of **2** was a priori surprising, since the first-level principle of electrostatic strain minimization leading to the trans geometry in **6** should also apply in **7b**. A kinetic argument might be first invoked, on the basis of the polarity of the solvent where the formation of the complexes took place: the relative proximity of the two positive charges of ligand **2** would indeed be more stabilized in acetonitrile ($\varepsilon_{20°C}$ = 37.5) than in dichloromethane ($\varepsilon_{20°C}$ = 9.1), where **7b** and **6** were respectively prepared. In the solid state, a thermodynamic rationale for the cis-chelation of **2** in **7b** can however be proposed on the basis of antisymbiotic effects on the trans influence at soft metal centers (referred to as "class b" metal atoms) such as Rh(I).[24]

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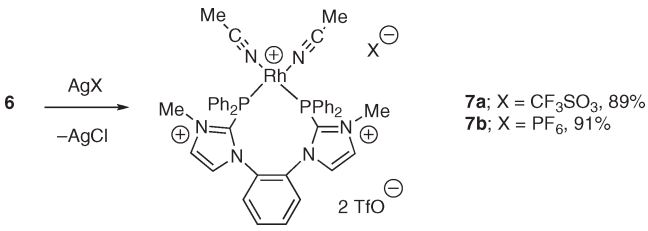
(24) On the relationships between the concepts of trans influence and HSAB antisymbiosis, see for example: (a) Pearson, R. G. *Inorg. Chem.* **1973**, *12*, 712. (b) Navarro, R.; Urriolabeitia, E. P. *J. Chem. Soc., Dalton Trans.* **1999**, 4111. (c) Harvey, J. N.; Heslop, K. M.; Orpen, A. G.; Pringle, P. G. *Chem. Commun.* **2003**, 278.

Scheme 5. Synthesis of Tricationic Rhodium Complexes **7a** and **7b** of the Bis(amidiniodiphosphane) Ligand **2**



The main difference between complexes **6** and **7b** resides in the number and the HSAB nature of the two nonphosphorus ligands. In complex **6**, three kinds of ligands are present: PPh_2R, $Cl^{(-)}$, and CO. Although the latter was early classified as a carbon-centered "soft base",[25] it is now well-established that the CO ligand acts more as an "acid" through its strong π-accepting character toward "class b" transition metals. Considering Pearson's quantitative global hardness, the conjugated oxygen atom actually makes CO much harder than chlorine (or chloride) and phosphines.[26] Within this "global" approximation, a prebonding HSAB analysis predicts that the hard CO ligand of **6** will select one of the softer $Cl^{(-)}$ or P(III) ligands in the trans position,[27] thus letting the electrostatic repulsion drive the trans-chelation of **2** and accommodating the trans-coordination of the Cl^- ligand. In complex **7b**, the globally hard MeCN ligands drive softer ligands to trans positions,[26] namely, the phosphorus atoms of **2**,[27] thus enforcing the cis-chelation of the latter. It is noteworthy that the HSAB justification indicated within the framework of the "global ligand" approximation is confirmed and refined by a "local softness" analysis.[28]

Another intriguing structural feature is the significant shortening of the P−Rh bonds by going from complexes **6** [2.2721(18), 2.2814(17) Å] to complex **7b** [2.2329(16), 2.2348 (17) Å]. This can be explained by the greater Lewis acidity of the cationic Rh^+ center in **7b** as compared to the neutral Rh(I) center in **6**, but also by the nature of the P and N donor atoms exhibiting different trans influences. Indeed, the P atom is a softer base than the N atom of the MeCN ligand and should exert a greater trans influence. And accordingly, the mutual P−*trans*-P arrangement in **6** results in larger Rh−P bond distances than the N−*trans*-P arrangement in **7** does.

Finally, the observed unusual geometrical features are accounted for by a compromise between competing effects of electrostatics, trans-antisymbiosis, and Lewis acidity.

Summary and Conclusion

The bis(amidiniophosphane) **2** was synthesized by an efficient short procedure and involved as a chelating ligand in three types of rhodium(I) complexes. In spite of the electrostatic strain induced by the proximal P-conjugated cationic charges of **2** and a possible positive charge at the rhodium center, the complexes **6**, **7a**, and **7b** are indefinitely stable in the solid state at room temperature and under an inert atmosphere. The residual donor character of ligand **2** was shown to be equivalent to that of a trialkylphosphite. In complex **6**, the original trans-chelating mode of **2** was attributed to the electrostatic repulsion which tends to move the two cationic charges of **2** away. The cis-chelation mode observed in the tricationic complex **7b** was shown to be consistent with the trans antisymbiosis principle surpassing the electrostatic constraint. The use of these complexes in catalytic processes requiring electron-poor ligands will be naturally envisioned. Preliminary results in this sense were previously communicated for the monocationic analogue **1** of **2**.[6]

Experimental Section

General Remarks. THF and diethyl ether were dried and distilled over sodium/benzophenone, pentane, dichloromethane, and acetonitrile over CaH_2. All other reagents were used as commercially available. All reactions were carried out under an argon atmosphere, using Schlenk and vacuum line techniques. Column chromatography was carried out on silica gel (60 Å, C.C 70−200 μm). The following analytical instruments were used: ^1H (Bruker ARX 250), ^{13}C (DPX 300), and ^{31}P (AV 500) NMR. NMR chemical shifts δ are in parts per million, with positive values to high frequency relative to the tetramethylsilane reference for ^1H and ^{13}C and to H_3PO_4 for ^{31}P. ^{103}Rh chemical shifts are given to high frequency from $\Xi(^{103}Rh) = 3.16$ MHz.

Synthesis of 4. To a solution of **3** (1.0 g, 4.76 mmol) in THF (200 mL) cooled to −78 °C was added *n*-butyllithium (2.5 M in hexane, 4.0 mL, 9.99 mmol). The suspension was then warmed to −20 °C and stirred for 2 h. After addition of chlorodiphenylphosphine (1.9 mL, 10.47 mmol) at −20 °C, the solution was stirred at room temperature for 3 h. After evaporation of the solvent under vacuum conditions, purification by chromatography on silica gel (CH_2Cl_2/AcOEt) of the residue gave **4** as a white solid (1.48 g, 54%). Recrystallization at room temperature from CH_2Cl_2/AcOEt afforded **4** as white crystals (mp 197−200 °C). ^1H NMR ($CDCl_3$, 25 °C): δ 7.44−7.46 (m, 2H, H_{ar}), 7.38−7.43 (m, 8H, H_{ar}), 7.33−7.37 (m, 12H, H_{ar}), 7.20 (brs, 2H, H_{ar}), 7.15−7.18 (m, 2H, H_{ar}), 6.89 (brs, 2H, H_{ar}). ^{13}C NMR ($CDCl_3$, 25 °C): δ 147.5 (d, J_{CP} = 4.2, C), 135.0 (brs, C), 134.2 (brs, C), 133.8 (m, CH_{ar}), 131.6 (s, CH_{ar}), 129.8 (brs, CH_{ar}), 129.6 (s, CH_{ar}), 129.2 (s, CH_{ar}), 128.5 (pseudo-t, J_{CP} = 3.7, CH_{ar}),

(25) Pearson, R. G *J. Chem. Educ*. **1968**, *45*, 581.

(26) Overall hardnesses have been indeed valuated in the order: $\eta(CO) = 7.9 > \eta(MeCN) = 7.5 > \eta(R_3P) = 6-4 \approx \eta(Cl^-) \approx \eta(Cl) \approx 4.7$ (in eV units): Pearson, R. G. *Inorg. Chem*. **1988**, *27*, 734.

(27) According to Pearson (ref 24): "*two soft ligands in mutual trans position will have a destabilizing effect on each other when attached to class b metal atoms*".

(28) The chemical interpretation of the "local softness" concept has been recently revisited (Torrent-Sucarrat, M.; De Proft, F.; Geerlings, P.; Ayers, P. W. *Chem. Eur. J*. **2008**, *14*, 8652). The atomic local softness s_x^{acid} and s_x^{base} can be determined by a finite difference approximation from the global softness S and the condensed Fukui indices f_X^+ and f_X^- identified for the corresponding variations of atomic, for example Mulliken, charges ($s_X = f_X S$). The latter have been calculated at the ab initio/6-3111G level for the CO molecule, for X = C and X = O (Lee, C.; Yang, W.; Parr, R. G. *THEOCHEM* **1988**, *163*, 305): $f_C^+ = 0.7666$, $f_C^- = 0.5984$ (the oxygen values can be deduced from $f_C^\pm + f_O^\pm = 1$). Using Pearson's experimental global value $S(CO) = 1/\eta(CO) = 1/7.9 = 0.1266$ eV,[24a] one obtains $s_C^{acid} = 0.0970$, $s_C^{base} = 0.0757$, $s_O^{acid} = 0.0295$, and $s_O^{base} = 0.0508$. The acidic and basic softnesses of the carbon atom are found to be similar. Although the CO ligand has been shown to be more accepting than donating (from 50/50 to 80/20),[23] the use of the average apolar Fukui indices $f_X^0 = 1/2(f_X^+ + f_X^-)$ is thus relevant for the present purpose. One deduces the corresponding average softnesses: $s_C^0 = 0.0864$ and $s_O^0 = 0.0402$. It is thus confirmed that carbon remains softer than oxygen, and that carbon is made harder by the bonded oxygen (for atomic carbon: $S(C) = 1/\eta(C) = 1/5.00 = 0.200$ eV).[24a] According to Pearson,[24a] the global (and local) softness of the monatomic $Cl^{(-)}$ is equal to $S(Cl) \approx S(Cl^-) = 1/\eta(Cl) = 1/4.68 = 0.214$ eV. The $Cl^{(-)}$ ligand is thus definitely softer than both the carbon of CO and the whole CO molecule. Assuming that $Cl^{(-)}$ and P atoms also have similar local softness values, the interpretation given within the global softness analysis remains the same.

123.5 (brs, CH_{ar}). ^{31}P NMR ($CDCl_3$, 25 °C): δ −30.5. MS (ESI+): m/z 579 $[M + H]^+$. HRMS (ESI^+) calcd for $C_{36}H_{29}N_4P_2$: 579.1867. Found: 579.1898.

Synthesis of 2 (2a and 2b). To a solution of **4** (1.52 g, 2.63 mmol) in CH_2Cl_2 (40 mL) cooled at −78 °C was added methyl trifluoromethanesulfonate (0.58 mL, 5.26 mmol). The suspension was then warmed to room temperature and stirred for 2 h. After evaporation of the solvent under vacuum conditions, the residue was washed with Et_2O (40 mL), affording a white solid as a mixture (71/29) of two isomers **2a** and **2b** (2.24 g, 94%). Recrystallization at 0 °C from CH_2Cl_2/Et_2O gave **2** as white crystals. NMR assignement: [a]major isomer (71%), [b]minor isomer (29%). ^1H NMR (CD_3CN, 25 °C): δ 7.98 (brs, 1H, H_{ar}), 7.84 (brs, 1H, H_{ar}), 7.80 (d, J_{HH} = 10.3, 3H, H_{ar}), 7.49−7.67 (m, 12H, H_{ar}), 7.29−7.45 (m, 8H, H_{ar}), 7.19 (m, 1H, H_{ar}), 3.41 (s, 6H, CH_3). ^{13}C NMR (CD_3CN, 25 °C): δ 145.8[b] (d, J_{CP} = 60.4, C), 145.6[a] (d, J_{CP} = 56.9, C), 134.7[b] (t, J_{CP} = 11.7, CH_{ar}), 134.3[a] (d, J_{CP} = 22.4, CH_{ar}), 133.3[a] (d, J_{CP} = 19.4, CH_{ar}), 133.2[a] (s, CH_{ar}), 133.1[b] (t, J_{CP} = 9.6, CH_{ar}), 132.2[b] (s, CH_{ar}), 131.7[b] (s, CH_{ar}), 131.6[a] (s, CH_{ar}), 131.3[a] (s, CH_{ar}), 131.0[a] (s, CH_{ar}), 130.7[a] (s, C_{ar}), 130.2[b] (brs, CH_{ar}), 130.0[a] (d, J_{CP} = 8.2, CH_{ar}), 129.9[b] (brs, CH_{ar}), 129.3[a] (s, CH_{ar}), 127.9[b] (s, C_{ar}), 127.7[b] (s, C_{ar}), 126.9[a] (s, C_{ar}), 126.8[a] (d, J_{CP} = 5.5, C_{ar}), 126.6[b] (d, J_{CP} = 8.1, CH_{ar}), 121.2 (q, J_{CF} = 320.8, CF_3SO_3), 38.7[b] (CH_3), 38.2[a] (CH_3). ^{31}P NMR (CD_3CN, 25 °C): δ −20.6[b]; −21.5[a]. MS (ESI+): m/z 757 $[M^{2+} - CF_3SO_3^-]^+$. HRMS (ESI^+) calcd for $C_{39}H_{34}N_4P_2O_3F_3S$: 757.1779. Found: 757.1702.

Synthesis of 5 and 6. A mixture of $[(RhCl(cod))_2]$ (0.27 g, 0.6 mmol) and dication **2** (1.0 g, 1.1 mmol) was dissolved in CH_2Cl_2 (30 mL) at 0 °C and stirred at room temperature for 6 h. After evaporation of the solvent, the crude residue was washed with Et_2O (40 mL), affording **5** as an orange solid. Then, complex **5** was dissolved in CH_2Cl_2 (30 mL), and carbon monoxide was bubbled for 30 min at room temperature. After evaporation of the solvent, and washing with Et_2O (20 mL), **6** was obtained as a yellow solid (0.85 g, 72%). Recrystallization at −20 °C from CH_3CN/Et_2O gave **6** as yellow crystals (mp 243−245 °C).

Complex **5**. ^1H NMR (CD_3CN, 25 °C): δ 7.17−7.85 (brs, H_{ar}), 3.89−5.50 (brs, CH_{cod}), 3.70 (brs, CH_3), 3.41 (brs, CH_3), 1.80−2.60 (brs, CH_{2cod}). ^{13}C NMR (CD_3CN, 25 °C): 123.3−141.5 (m, C_{ar}, CH_{ar}), 108.1 (brs, CH_{ar}), 75.6 (brs, CH_{cod}), 72.4 (brs, CH_{cod}), 40.1 (brs, CH_3), 28.8−32.2 (brs, CH_{2cod}). ^{31}P NMR (CD_3CN, 25 °C): δ +33.4 (brd, J_{PRh} = 153.9). MS (ESI+): m/z 1003 $[M - TfO]^+$.

Complex **6**. ^1H NMR (CD_3CN, 25 °C): δ 8.15 (brs, 2H, H_{ar}), 8.07−8.11 (brm, 4H, H_{ar}), 7.84−7.87 (m, 2H, H_{ar}), 7.70−7.76 (m, 10H, H_{ar}), 7.60−7.64 (m, 6H, H_{ar}), 7.14−7.18 (m, 2H, H_{ar}), 6.99−7.02 (m, 2H, H_{ar}), 3.44 (s, 6H, CH_3). ^{13}C NMR (CD_3CN, 25 °C): 185.1 (td, J_{CRh} = 74.2, J_{CP} = 15.3, CO), 146.1 (t, J_{CP} = 16.0, C), 138.1 (brs, CH_{ar}), 134.1 (s, CH_{ar}), 133.8 (brs, CH_{ar}), 133.3 (s, CH_{ar}), 132.0 (s, CH_{ar}), 131.5 (s, CH_{ar}), 131.3 (s, C); 130.2 (t, J_{CP} = 5.9, CH_{ar}), 129.8 (t, J_{CP} = 5.8, CH_{ar}), 129.4 (s, CH_{ar}), 127.4 (t, J_{CP} = 27.3, C), 127.3 (t, J_{CP} = 27.3, C), 127.4 (s, CH_{ar}), 123.1 (t, J_{CP} = 21.6, C), 121.2 (q, J_{CF} = 321.9, CF_3SO_3), 39.5 (s, CH_3). ^{31}P NMR (CD_3CN, 25 °C): δ +31.3 (J_{PRh} = 133.7). ^{103}Rh NMR (CD_3CN, 25 °C): δ −299. MS (ESI+): m/z 923 $[M - TfO]^+$. HRMS (ESI^+) calcd for $C_{40}H_{34}N_4O_4F_3P_2SClRh$: 923.0472. Found: 923.0557.

Synthesis of 7a and 7b. A mixture of a silver salt AgX (X = TfO, PF_6; 0.30 mmol) and **6** (0.22 g, 0.20 mmol) was dissolved in CH_3CN (10 mL) at −40 °C and then stirred at room temperature for 12 h. After filtration of the solid, the solution was evaporated under vacuum conditions, and the residue was washed with Et_2O (20 mL). Complex **7a** was obtained as an oily residue (X = TfO, 0.21 g, 89%). Recrystallization of complex **7b** (X = PF_6, 0.21 g, 91%) at −20 °C from CH_3CN/Et_2O afforded orange crystals (mp 218−220 °C).

Complex **7a**. ^1H NMR (CD_3CN, 25 °C): δ 8.32 (s, 2H, H_{ar}), 8.04 (s, 2H, H_{ar}), 7.82−7.91 (m, 4H, H_{ar}), 7.45−7.75 (m, 10H, H_{ar}), 7.30−7.39 (m, 6H, H_{ar}), 7.10−7.14 (m, 4H, H_{ar}), 3.33 (s, 6H, CH_3). ^{13}C NMR (CD_3CN, 25 °C): 139.2 (pseudo t, J_{CP} = 13.3, C), 134.4 (t, J_{CP} = 7.5, CH_{ar}), 133.2 (s, CH_{ar}), 133.0 (s, CH_{ar}), 132.4 (t, J_{CP} = 5.7, CH_{ar}), 132.1 (s, CH_{ar}), 130.8 (s, CH_{ar}), 130.4 (s, C), 130.1 (s, CH_{ar}), 129.7 (d, J_{CP} = 10.1, CH_{ar}), 129.6 (d, J_{CP} = 11.3, CH_{ar}), 129.3 (s, CH_{ar}), 128.5 (pseudo t, J_{CP} = 28.3, C), 124.8 (pseudo t, J_{CP} = 26.4, C), 121.1 (q, J_{CF} = 320.8, CF_3SO_3), 40.0 (s, CH_3). ^{31}P NMR (CD_3CN, 25 °C): δ +35.6 (J_{PRh} = 178.2). ^{103}Rh NMR (CD_3CN, 25 °C): δ +247. MS (ESI+): m/z 1009 $[M - TfO]^+$. HRMS (ESI^+) calcd for $C_{40}H_{34}N_4O_6F_6P_2S_2Rh$: 1009.0354. Found: 1009.0454.

Complex **7b**. ^1H NMR (CD_3CN, 25 °C): δ 8.21 (s, 2H, H_{ar}), 8.00 (d, J_{HH} = 1.9, 2H, H_{ar}), 7.89−7.91 (m, 2H, H_{ar}), 7.80−7.82 (m, 2H, H_{ar}), 7.64−7.71 (m, 6H, H_{ar}), 7.46−7.50 (m, 4H, H_{ar}), 7.41 (t, J_{HH} = 7.4, 2H, H_{ar}), 7.29 (t, J_{HH} = 7.2, 4H, H_{ar}), 7.10−7.14 (m, 4H, H_{ar}), 3.34 (s, 6H, CH_3). ^{13}C NMR (CD_3CN, 25 °C): 139.3 (pseudo t, J_{CP} = 12.6, C), 134.4 (t, J_{CP} = 7.1, CH_{ar}), 133.3 (s, CH_{ar}), 133.0 (s, CH_{ar}), 132.4 (t, J_{CP} = 5.6, CH_{ar}), 132.2 (s, CH_{ar}), 130.8 (s, CH_{ar}), 130.4 (s, C), 130.1 (s, CH_{ar}), 129.7 (d, J_{CP} = 11.0, CH_{ar}), 129.6 (d, J_{CP} = 11.1, CH_{ar}), 129.2 (s, CH_{ar}), 128.4 (pseudo t, J_{CP} = 27.7, C), 124.6 (pseudo t, J_{CP} = 25.2, C), 121.1 (q, J_{CF} = 320.7, CF_3SO_3), 40.1 (s, CH_3). ^{31}P NMR (CD_3CN, 25 °C): δ +35.7 (J_{PRh} = 178.3). ^{103}Rh NMR (CD_3CN, 25 °C): δ +400. MS (ESI+): m/z 1005 $[M - TfO]^+$. HRMS (ESI^+) calcd for $C_{39}H_{34}N_4O_3F_9P_3SRh$: 1005.0476. Found: 1005.0527.

Electrochemistry Data. Voltammetric measurements were carried out with a potentiostat Autolab PGSTAT100. Experiments were performed at room temperature in a homemade airtight three-electrode cell connected to a vacuum/argon line. The reference electrode consisted of a SCE separated from the solution by a bridge compartment. The counter electrode was a platinum wire of ca. 1 cm^2 apparent surface. The working electrode was a Pt microdisk (0.5 mm diameter). Voltammograms were recorded in a dry CH_3CN solution (ca. 3×10^{-3} M) in the presence of 0.1 M *n*-tetrabutylammonium hexafluorophosphate as the supporting electrolyte, under nitrogen at 25 °C.

Crystal Structure Determination of Compounds 6 and 7b. For complex **6**, data were collected at a low temperature (180 K) on an Xcalibur Oxford Diffraction diffractometer using a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and equipped with an Oxford Instrument Cooler Device. The final unit cell parameters have been obtained by means of a least-squares refinement. The structures have been solved by Direct Methods using SIR92 and refined by means of least-squares procedures on F using the program Crystal. The atomic scattering factors were taken from international tables for X-ray crystallography. All hydrogen atoms were geometrically placed and refined by using a riding model.

For complex **7b**, data were collected at a low temperature (110 K) on a Bruker Kappa Apex II diffractometer using a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and equipped with an Oxford Cryosystems Cryostream Cooler Device. The final unit cell parameters have been obtained by means of a least-squares refinement performed on a set of 9126 well-measured reflections. The structures have been solved by direct methods using SIR92 and refined by means of least-squares procedures on F^2 with the aid of the program SHELXL97, included in the software package WinGX, version 1.63. The atomic scattering factors were taken from international tables for X-ray crystallography. All hydrogen atoms were located geometrically and refined by using a riding model. All non-hydrogen atoms were anisotropically refined, and in the last cycles of refinement, a weighting scheme was used, where weights are calculated from the following formula: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. Drawings

of molecules were performed with the program ORTEP32, with 30% probability displacement ellipsoids for non-hydrogen atoms.

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