New Arylruthenium(II) Complexes of the *P,C,P′*-Coordinating Terdentate Monoanionic Aryl Ligands $[C_6H_2(CH_2PPh_2)_2$-2,6-R-4$]^-$ (PCP-R-4; R = Ph, H). Synthesis of 16-Electron Species $[Ru^{II}X$(PCP-R-4)$(PPh_3)]$ (X = Cl, I, OTf) and Their Reactivity toward the Neutral Terdentate N-Donor Ligand 2,2′:6′,2″-Terpyridine (terpy)

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The synthesis and characterization of new, five-coordinate, diamagnetic, 16-electron arylruthenium(II) complexes $[Ru^{II}X\{C_6H_2(CH_2PPh_2)_2$-2,6-R-4$\}(PPh_3)]$ (**1**, X = Cl, R = H; **2**, X = Cl, R = Ph; **3**, X = OSO_2CF_3, R = H; **4**, X = I, R = H) are described. These coordinatively unsaturated complexes contain a stable C_{aryl}−Ru σ-bond resulting from *pseudo*meridional terdentate *P,C,P′*-bonding of the monoanionic $\{C_6H_2(CH_2PPh_2)_2$-2,6-R-4$\}^-$ ligand (general abbreviation PCP-R-4; for R = H and R = Ph, abbreviated as PCP and PCP-Ph, respectively) that also provides two P → Ru bonds. This bonding mode of the PCP-R-4 ligands adopted in complexes **1**−**4** means that these species are structurally closely related to the complexes $[RuCl\{C_6H_2(CH_2NMe_2)_2$-2,6-R-4$\}(PPh_3)]$ (R = H, Ph) in which there is terdentate *N,C,N′*-coordination. Complexes **1** and **2** were synthesized *via* cyclometalation reactions of the respective neutral diphosphine compounds $C_6H_3(CH_2PPh_2)_2$-2,6-R-4 (general abbreviation PC(H)P-R-4; for R = H and R = Ph, abbreviated as PC(H)P and PC(H)P-Ph, respectively) with $[Ru^{II}Cl_2(PPh_3)_4]$. The complex $[Ru^{II}$(OTf)(PCP)$(PPh_3)]$, **3**, prepared by reaction of **1** with AgOTf (OTf = OSO_2CF_3 = triflate), has the triflate anion bound to ruthenium in noncoordinating solvents. On the NMR time scale complex **3** in solution exhibits temperature-dependent fluxionality that is associated with reversible changes of the complex stereochemistry. The triflate PCP complex **3** reacts cleanly with the neutral N-donor ligand 2,2′:6′,2″-terpyridine (terpy) to afford $[Ru^{II}$(PCP)(terpy)$][OTf]$, **5**. However, whereas the reaction of terpy with the PCP-Ph complex **2** affords $[Ru^{II}$(PCP-Ph)(terpy)$]Cl$, **6**, its reaction with PCP chloro complex **1** generates a mixture of products. These reactivities of PCP and PCP-Ph complexes (**1**−**3**) toward terpy are compared and contrasted with those of related ruthenium complexes containing the monoanionic aryldiamine ligand $\{C_6H_2(CH_2NMe_2)_2$-2,6-R-4$\}^-$ (abbreviated as NCN-R-4).

Introduction

The potentially *N,C,N′*-terdentate monoanionic aryl ligand $[C_6H_3(CH_2NMe_2)_2$-2,6$]^-$ (NCN = 2,6-bis[(dimethylamino)methyl]phenyl)[1] and the related anionic *P,C,P′*-coordinating bis(phosphine) ligand $[C_6H_3(CH_2PPh_2)_2$-2,6$]^-$ (PCP = 2,6-bis[(diphenylphosphino)methyl]-phenyl),[2−4] depicted in Scheme 1, have attracted considerable interest as tools both for controlling the reactivity of metal centers in a variety of transition metal complexes and for stabilizing complexes in unusual geometries. For example, intermediates in oxidative addition reactions of I_2 and MeI to the Pt^{II}(NCN) moiety have been stabilized as isolable complexes.[5,6] Furthermore, the complexes [NiX(NCN)] and various derivatives can be used as homogeneous catalysts in the Kharasch addition reaction, *i.e.* the addition of polyhalogenated alkanes to alkenes with the formation of new C−C and C−X (X = halogen) bonds.[7] Recently, it has been found that certain manganese and tantalum complexes containing NCN as a ligand also exhibit interesting catalytic activity in cross-coupling reactions of functionalized alkyl halides with alkyl Grignard

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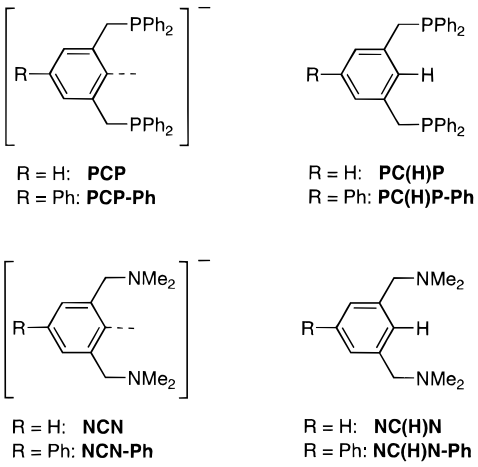
Scheme 1. Abbreviations for Monoanionic Ligands and Ligand Precursors



reagents and in ring-opening metathesis polymerization reactions of cyclic alkenes, respectively.[8]

The aryl nucleus of NCN and PCP lends itself to derivatization, and the family of substituted ligands $[C_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}R\text{-}4]^-$ (NCN-R-4) and $[C_6H_2(CH_2PPh_2)_2\text{-}2,6\text{-}R\text{-}4]^-$ (PCP-R-4), Scheme 1, appears to offer interesting potential. It is to be anticipated that the bonding of these ligands of general formula $[C_6H_2(CH_2ER'_2)_2\text{-}2,6\text{-}R\text{-}4]^-$ (ER'_2 = NMe_2 or PPh_2) will normally comprise a C_{aryl} to metal σ-bond which is complemented by intramolecular coordination of the donor atoms of the two ER'_2 groups to afford a meridional geometry; with NCN the N−M−N angles are then typically 145−165°.[1] With this geometry the metal center is embedded in an organic cleft, and it is clear that the electronic and steric properties of the complex will be sensitive to the nature of both the heteroatomic ER'_2 group and the *para* substituent R on the aryl ring. The latter was clearly demonstrated by the series of complexes [NiX(NCN-R-4)] (R = NMe_2, Me, H, Cl, C(O)Me), whose catalytic and redox properties could be electronically tuned by variation of the group R *para* to the C_{ipso}−Ni bond.[7,9]

In an extension of our work to ruthenium complexes with either *N,C,N′*- or *P,C,P′*-coordinating ligands we have been able to isolate stable mononuclear aryldiamine complexes with the specific NCN-R-4 ligands in which R is H (NCN)[10a] or Ph (NCN-Ph),[10b] and we have already reported interesting bimetallic complexes which result from oxidative C−C coupling reactions of some of these species.[11] It is worth noting that platinum complexes containing chiral derivatives of PCP as ligands have been successfully synthesized.[12] Significantly, some of the 16-electron NCN-R-4 ruthenium complexes efficiently catalyze hydrogen-transfer reactions such as the reduction of ketones to alcohols in the presence of base with 2-propanol as the reducing agent.[13]

The first synthesis of complexes [RuCl(NCN-R-4)(PPh_3)][10b] and the interesting preliminary data we obtained for their reactivity as catalysts in hydrogen transfer and hydrogenation reactions[13] have now prompted us to investigate closely related complexes based on the PCP ligand and its derivatives. This publication, which deals principally with the synthesis and characterization of ruthenium complexes of two anionic PCP-R-4 ligands, i.e. $[C_6H_3(CH_2PPh_2)_2\text{-}2,6]^-$ $(PCP)^{2-4}$ and novel $[C_6H_2(CH_2PPh_2)_2\text{-}2,6\text{-}Ph\text{-}4]^-$ (PCP-Ph), illustrates the important role that auxiliary ligands play in determining the nature of Ru(II) species containing such terdentate ligand systems. We also present the first direct comparison of the influence of *N,C,N′*- and *P,C,P′*-bonding in the chemistry of structurally closely related ruthenium complexes containing terdentate ligands $[C_6H_2(CH_2ER'_2)_2\text{-}2,6\text{-}R\text{-}4]^-$ (ER'_2 = NMe_2, PPh_2) and correlate these differences with both steric and electronic influences.

Results

The known diphosphine compound $C_6H_4(CH_2PPh_2)_2$-1,3 (PC(H)P)[2b] reacts in CH_2Cl_2 with $[Ru^{II}Cl_2(PPh_3)_4]$[14] to afford, in a direct cyclometalation reaction, the five-coordinate complex [RuCl(PCP)(PPh_3)], **1**, that has been isolated in moderate yield as a green, air-sensitive solid. On the basis of its characteristic ^1H, ^{13}C, and ^{31}P NMR data in CD_2Cl_2, **1** is proposed to have a square-pyramidal geometry, with the PPh_3 ligand occupying the apical position as illustrated in Scheme 2. In the ^1H NMR spectrum of **1** one observes, for example, diastereotopic benzylic hydrogen atoms indicative of the absence of a molecular symmetry plane through the benzylic carbon atoms. Furthermore, in the ^{31}P NMR spectrum there is a small coupling between the two equivalent PPh_2 groups of PCP and the PPh_3 ligand ($^2J(PP)$ = 31.7 Hz) indicative of the PPh_3 ligand being positioned *cis* to both PPh_2 groups. In the ^{13}C NMR spectrum of **1** the C_{ipso} atom affords a doublet resonance arising from coupling to the PPh_3 group ($^2J(CP)$ = 16.6 Hz); the low magnitude of this coupling constant is in accordance with an angle C_{ipso}−Ru−PPh_3 that deviates considerably from 180°. The absence of coupling between the P atoms of PCP and C_{ipso} suggests they are both positioned *cis* to C_{ipso} as expected for a *pseudo*meridional *P,C,P′*-binding geometry. The proposed structure for **1** is analogous to the square-pyramidal structure previously reported for the related NCN iodo complex [RuI(NCN)(PPh_3)].[10a]

The course of the reaction of the diphosphine PC(H)P with $[RuCl_2(PPh_3)_3]$/PPh_3 (that has to involve a cyclometalation step)[12] was followed by ^{31}P NMR spectroscopy and is depicted in Figure 1. Early in the reaction

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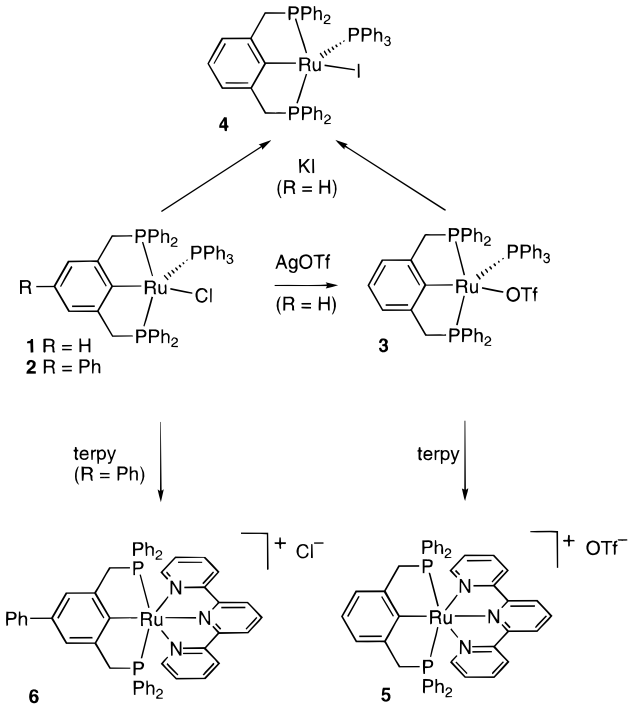
(13) For example, it proved possible to reduce cyclohexanone to cyclohexanol with conversions of better than 90% at a substrate to catalyst ratio as high as 2000:1. Moreover, such complexes also catalyze the selective reduction by dihydrogen of an activated C=C bond in alkenes such as benzylideneacetone: Karlen, T.; van Koten, G. Manuscript in preparation.

(14) It is known that $[RuCl_2(PPh_3)_4]$ in solution is predominantly present as $[RuCl_2(PPh_3)_3]$ (+PPh_3) due to ligand dissociation processes: (a) Hallman, P. S.; Stephenson, T. A.; Wilkinson, G. *Inorg. Synth.* **1970**, *XII*, 237. (b) Hoffman, P. R.; Caulton, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 4221.

Scheme 2. Synthesis Overview



a new set of signals consisting of a triplet (84.05 ppm, $^2J(PP) = 31.6$ Hz) and a doublet (39.51 ppm, $^2J(PP) = 31.6$ Hz) appear. The loss of intensity of this set of signals with time was proportional to the intensity gain of the resonances belonging to the end product **1**, and these resonances have been assigned to an as yet unidentified species **I**. The "triplet + doublet" pattern is consistent with **I** containing two chemically equivalent phosphorus nuclei coupled to one chemically distinct phosphorus atom, and in this respect one can see that the chemical shifts and the coupling constants of the resonances belonging to **I** are very similar to those of **1**. We believe that this species may be dinuclear, but unfortunately, when all of the starting material [$Ru^{II}Cl_2(PPh_3)_4$] has reacted to **I**, the final product **1** is already present to such a degree that it has not proved possible to isolate this species in a pure form.

In a synthesis analogous to the one described for the preparation of **1**, the new neutral diphosphine compound $C_6H_3(CH_2PPh_2)_2$-1,3-Ph-5 (PC(H)P-Ph; see Experimental Section) reacts with [$Ru^{II}Cl_2(PPh_3)_4$] to afford [Ru^{II}Cl(PCP-Ph)(PPh_3)], **2**. The NMR data of **2** are very similar to those obtained for **1**, though with the anticipated changes in resonance patterns that result from the presence of a phenyl group, rather than a proton, positioned *para* to C_{ipso}. On the basis of spectroscopic and microanalytical data, complex **2** is postulated to be a mononuclear square-pyramidal complex, isostructural with **1**, as depicted in Scheme 2.

Although complexes **1** and **2** are 16-electron, five-coordinate species, i.e. coordinatively unsaturated, in solution, they show no fluxional behavior on the NMR time scale at room temperature either in noncoordinating solvents such as benzene and CH_2Cl_2 or in the potentially coordinating solvent THF.

Addition of an equimolar amount of AgOTf (OTf = OSO_2CF_3 = triflate) to PCP complex **1** in dichloromethane results in replacement of the chloride ligand by the OTf monoanion to afford the green, air-sensitive

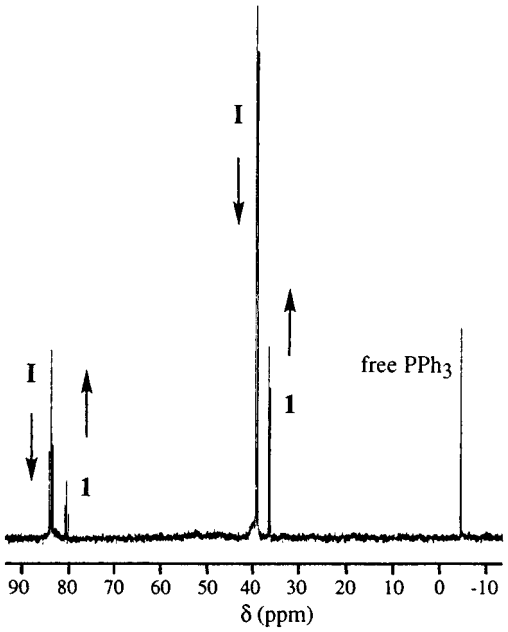
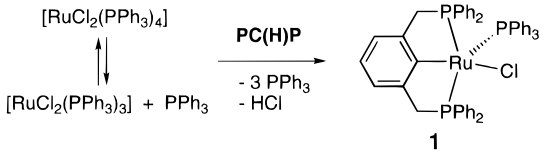


Figure 1. ^{31}P NMR spectrum (CD_2Cl_2) of the reaction mixture of PC(H)P with [$RuCl_2(PPh_3)_3$]/PPh_3 that affords **1** via species **I**.

Scheme 3. Synthesis of 1



complex [Ru(OTf)(PCP)(PPh_3)], **3** (Scheme 2). In CH_2Cl_2 the ^{31}P NMR spectrum at 298 K consists of a slightly broadened signal (for the PPh_3 ligand) and a sharp doublet resonance, but at 220 K the resonances have shifted significantly and the spectrum consists of a triplet and a doublet with a $^2J(PP)$ coupling constant of 31.7 Hz. The low value of $^2J(PP)$ indicates that the PCP ligand has preserved a *pseudo*meridional binding mode with an associated *cis* arrangement between the PPh_2 and the PPh_3 groups. Moreover, a low-temperature (LT) ^1H NMR spectrum shows diastereotopic benzylic hydrogens, and a LT ^{13}C NMR (CD_2Cl_2) spectrum reveals a doublet for C_{ipso} with a small $^2J(CP)$ of 17 Hz. From these data it can be concluded that **3** has, like **1**, a mutual *cis* arrangement of C_{ipso} and the PPh_3 which is retained at low temperature. The temperature-dependent changes in the spectra of **3** point to fluxional behavior that we believe may be associated with η^1-O-to-η^2-O,O′ binding of the triflate anion.

Alternative processes involving dissociation of the OTf group to form a 14-electron four-coordinate ionic species seem unlikely (particularly in toluene), and the absence of effective bridging ligands in combination with the steric bulk of the PPh_2 groups and the PPh_3 ligand (see Discussion) would seem to exclude associative intermolecular processes that involve dimer formation or solvent coordination. We wished to investigate this process further but the poor solubility of **3** in toluene at low temperature has hampered NMR studies in this solvent.

Surprisingly, although the ^{31}P NMR spectrum of **3** in the coordinating solvent THF at room temperature was simple, at low temperature the spectrum comprises a complex set of signals that indicates a situation in which

one or more THF molecules have added to the coordinatively unsaturated complex **3** to afford a mixture of products.

The iodo complex [RuI(PCP)(PPh_3)], **4** (Scheme 2), has been obtained by two different synthetic routes. In the first route chloro complex **1** is reacted with an excess of KI in MeOH at reflux for 4 days. The second route involves the conversion of triflate complex **3** with an equimolar amount of KI in MeOH, and this procedure affords **4** in high yield within a few hours at room temperature. Since ^{1}H, ^{13}C, and ^{31}P NMR data for **4** are very similar to those obtained for the chloro complex **1**, we conclude that these two complexes are analogous and isostructural.

Reaction of 2,2′:6′,2″-terpyridine (terpy) with the PCP complexes **1**−**3** affords new products of the type [Ru(PCP-R)(terpy)]X. The red, air-stable ionic complex [Ru(PCP)(terpy)][OTf], **5**, which is formed readily within a few hours from triflate complex **3** and terpy in MeOH at reflux, has been fully characterized by NMR spectroscopy in CD_2Cl_2 and elemental microanalysis. The ^{1}H NMR spectrum of **5** shows equivalent benzylic hydrogens, indicative of a molecular mirror plane containing the benzylic carbon atoms. Only one singlet resonance (for PCP) is found by ^{31}P NMR spectroscopy, so confirming the absence of a PPh_3 ligand. In the ^{13}C NMR spectrum of this species there is a singlet resonance for C_{ipso}, consistent with the two equivalent PPh_2 groups being in a *cis* position to C_{ipso}. The overall structure is thus believed to be an ionic one with a triflate anion and a complex monocation having a six-coordinate Ru(II) center (see Scheme 2).

In contrast, if chloro PCP complex **1** is reacted with 1 equiv of terpy in MeOH at reflux a mixture of products is obtained of which approximately 60% (based on ^{31}P NMR data) can be attributed to the complex [Ru(PCP)(terpy)]Cl, but unfortunately, attempts to purify this product by column chromatography or by exchange of the counterion failed.

However, the chloro PCP-Ph complex **2** reacts, albeit slowly but in a well-defined way, with terpy in MeOH at reflux to afford within 2 days the red, air-stable complex [Ru(PCP-Ph)(terpy)]Cl, **6**, as the only product. The spectroscopic data for **6** are similar to those obtained for **5** and are consistent with the ionic structure depicted schematically in Scheme 2. The ^{13}C NMR spectrum of **6** was particularly useful for characterizing this complex since it showed in the aromatic region all the expected resonances (Experimental Section). Attempts to prepare ionic terpy complexes like **5** and **6** directly *via* a cyclometalation reaction between $[Ru^{III}(O{=}CMe_2)_3(terpy)][X]_3$ (X = BF_4, OTf) and PC(H)P or PC(H)P-Ph were partially successful and afforded, as judged by ^{31}P NMR spectroscopy, ca. 30−50% of the desired material in the product mixture, though it did not prove possible to isolate pure products from these mixtures.

Discussion

General Observations. We have now shown that it is possible with the diphosphine monoanionic ligands $[C_6H_2(CH_2PPh_2)_2$-2,6-R-4$]^-$ to prepare 16-electron Ru(II) complexes [RuCl(PCP-R)(PPh_3)] that are analogous to complexes [RuCl(NCN-R)(PPh_3)] containing the aryldiamine system $[C_6H_2(CH_2NMe_2)_2$-2,6-R-4$]^-$ (Scheme 1). This affords an unprecedented opportunity to examine differences between N-donor ($-NMe_2$) and P-donor ($-PPh_2$) ligand sites in terms of electronic and steric influence on ruthenium(II) species. These differences should be quite pronounced because of the different sizes of the heteroatoms as well as the fact that the NMe_2 and the PPh_2 groups contain very different substituents (alkyl vs aryl). We have already reported that late transition metal complexes with anionic ligands $[C_6H_3(CH_2NR'R'')_2$-2,6$]^-$ are most easily formed when the substituents R′ and R″ are both Me, i.e. NCN.[1] Compared to NCN those ligands with amine groups $-NEt_2$, $-NMeEt$, $-NMe(^iPr)$, and $-NMe(^tBu)$,[15] as well as with pyrrolidine[7c] and proline[16] ring systems, are expected to have nitrogen donor atoms that are stronger Lewis bases, but the ability of these groups to coordinate is severely influenced by steric factors. Compared to phosphorus, nitrogen has a relatively small atomic radius, and therefore N-donor ligands have larger cone angles than their phosphorus analogs.[1] This difference explains why a ligand like 1,3-bis[(di-*tert*-butylphosphino)methyl]benzene (PCP-^{t}Bu),[17] despite its apparent significant bulk, can form not only four-coordinate complexes of Pd, Pt, Ni, and Rh but also six-coordinate Ir and Rh species when small auxiliary ligands (e.g. CO, Cl, etc) are present.[14b,17,18] For the aryldiamine systems $[C_6H_3(CH_2NR'R'')_2$-2,6$]^-$ also electronic effects of the R′ and R″ substituents play a much larger role than in related phosphine chemistry. For example, the $-NMe(Ph)$ group of the ligand $[C_6H_3(CH_2NMe(Ph))_2$-2,6$]^-$ is found to be a poor N-donor (i.e. weak Lewis base) group because of electron delocalization of the lone pair and this group is unable to substitute PEt_3 in the complex $[NiCl\{C_6H_3(CH_2NMe(Ph))_2$-2,6$\}(PEt_3)_2]$ so that this aryldiamine ligand is only monodentate η^1-*C*-bonded to nickel and the nonbonded N-atoms have a trigonal planar geometry.[15]

Formation of PCP-R-4 Complexes. The differences between heteroatom donor groups are apparent both in the formation of complexes $[RuCl\{C_6H_2(CH_2ER'_2)_2$-R-4$\}(PPh_3)]$ (ER'_2 = NMe_2, PPh_2) and in their physical characteristics and reactivity. So far all attempts to synthesize NCN-R-4 ruthenium complexes *via* cyclometalation reactions have failed, so that in practice the synthesis of NCN ruthenium complexes requires a transmetalation reaction of (2,6-bis[(dimethylamino)methyl]phenyl)lithium with a suitable Ru(II) starting material.[10]

This paper has shown that complexes $[Ru^{II}Cl(PCP$-R-4$)(PPh_3)]$ are readily accessible by a cyclometalation route. In the general mechanism of a cyclometalation reaction that results in the potential formation of $[RuCl\{C_6H_2(CH_2ER'_2)_2$-R-4$\}(PPh_3)]$ species, as shown in Scheme 4, it is the nature of the ruthenium starting material and the coordinative property of $-NMe_2$ *vs* $-PPh_2$ which are of primary importance; the nature of the C−H bond to be metalated is similar in both PC(H)P-R-4 and NC(H)N-R-4.

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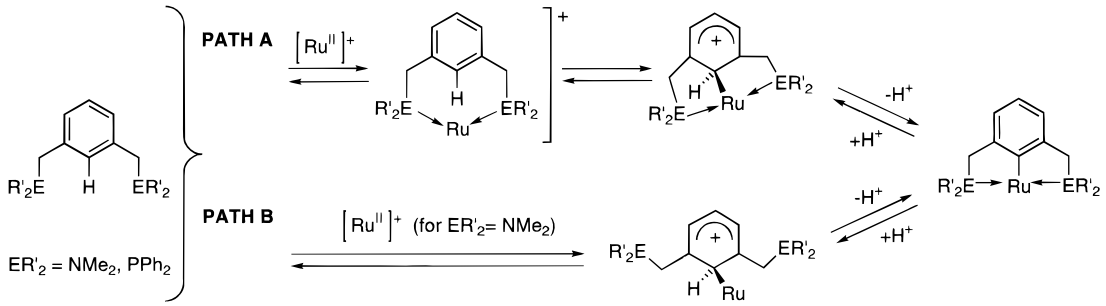
Scheme 4. Cyclometalation Routes A and B



The first route for cyclometalation (Scheme 4, path A) involves prior coordination of the heteroatom donor sites to ruthenium, and this assists subsequent attack of the coordinated metal center to the appropriately positioned arene C−H bond;[12,17] this route is the one that is responsible for the formation of ruthenium PCP-R-4 complexes. Since NC(H)N fails to cyclometalate with $[RuCl_2(PPh_3)_3]$/PPh_3 (in solution),[14] we conclude that this neutral aryldiamine is less effective than PC(H)P-R in replacing the PPh_3 ligands in this starting material.

A second route for cyclometalation (Scheme 4, path B) would comprise an electrophilic attack of the metal center on the aryl ligand with direct formation of an arenonium intermediate. In such an intermediate (where the M−C bond is ortho to the "free" heteroatom-containing substituents) further reaction involving removal of H^+ can be assisted by the heteroatoms.[19,20] However, this route seems only to be viable in the case of NC(H)N. For the PC(H)P ligand electrophilic attack of a metal center on an arene C−H bond is prevented by strong inter- and intramolecular ligation of the excess of phosphorus donor atoms (of both PPh_3 and the $-PPh_2$ groups) that is present.

Our view that route A is responsible for the formation of the PCP ruthenium complexes is supported by the fact that it is only the C−H bond between the two CH_2PPh_2 arms (position 2) of PC(H)P that is metalated, even though the outside positions (4 and 6) are sterically less hindered. The driving force for the displacement of three PPh_3 ligands from $[RuCl_2(PPh_3)_3]$/PPh_3 for one PC(H)P molecule is likely to be the property of this bis(phosphine)[14b] to act as a neutral *pseudo* trans-spanning ligand. As shown in Scheme 4, the resulting schematic intermediate in route A has the C_{ipso}−H bond forced close to the ruthenium center whereby C−H activation is facilitated.

Spectroscopic Aspects of PCP-R-4 and NCN-R-4 Complexes. The electronic characteristics of the PCP complex **1** were expected to differ from those of the corresponding NCN complex $[RuCl(NCN)(PPh_3)]$ since each of the $-NMe_2$ ligating groups has almost exclusively σ-donating properties whereas the P-donor center in the $-PPh_2$ group can have both electron-donating and electron-accepting character, i.e. the $-PPh_2$ groups attenuate their donating effect by accepting electron density from ruthenium *via* back-donation from the metal center into low-lying empty phosphorus-based orbitals. These electronic factors account for the fact that $[RuCl(NCN)(PPh_3)]$ has in its UV/vis spectrum a λ_{max} at 557 nm (ϵ = 1287 M^{-1} cm^{-1})[10a] whereas the corresponding green PCP complex **1** has a λ_{max} at 630 nm (ϵ = 1250 M^{-1} cm^{-1}); in a qualitative outline back-donation into the $-PPh_2$ groups leads to a smaller MLCT (metal to ligand charge transfer) bandgap in **1** and therefore to a shift of this transition to lower frequency.

Table 1. ^{31}P and ^{13}C NMR Data for PCP-R-4 and NCN-R-4 Ruthenium Complexes[a]

Ru species	^{31}P NMR, δ (ppm) PPh_2	PPh_3	^{13}C NMR, δ (ppm) C_{ipso} (^2J(CP))[b]
PCP-R-4 Complexes			
$[RuCl(PCP)(PPh_3)]$, **1**	36.5	81.3	172.7 (16.6)
$[RuCl(PCP\text{-}Ph)(PPh_3)]$, **2**	36.7	80.8	173.2 (17.3)
$[Ru(OTf)(PCP)(PPh_3)]$, **3**	38.2[c]	75.9[c]	164.6 (17.0)
$[RuI(PCP)(PPh_3)]$, **4**	36.2	77.2	177.3 (16.0)
[Ru(PCP)(terpy)][OTf], **5**	42.5		183.5 (s)
[Ru(PCP-Ph)(terpy)]Cl, **6**	42.7		182.3 (s)
NCN-R-4 Complexes			
$[RuCl(NCN)(PPh_3)]$[d]		91.1	185.8 (15.3)
$[RuCl(NCN\text{-}Ph)(PPh_3)]$[e]		90.4	186.6 (16)
$[RuI(NCN)(PPh_3)]$[d]		89.0	187.2 (14.1)

[a] Measured in CD_2Cl_2. Chemical shifts referenced to external standard H_3PO_4 (^{31}P NMR) or TMS (^{13}C NMR). [b] Coupling constant between C_{ipso} and PPh_3 in Hz. All C_{ipso} resonances are doublets unless indicated otherwise. [c] Broad resonances at room temperature. Data at 220 K: $\delta(PPh_3)$ 78.9 ppm; $\delta(PPh_2)$ 36.7 ppm. [d] From ref 10a. [e] From ref 10b.

The ^{31}P NMR data for the PPh_3 ligands and $-PPh_2$ groups in the ruthenium PCP-R-4 complexes **1**−**6** (collected in Table 1) together with data for PPh_3 ligands in some related NCN-R species clearly reflect changes in the electronic and steric influences operative at and around the metal center. For example one notices that the $-PPh_2$ resonances move to higher ppm values (i.e. the P atoms become more deshielded) through the introduction of π-electron-accepting groups (e.g terpy) or by the removal of σ-electron-donating groups (e.g. Cl^-) and that in general these resonances are less sensitive than those of PPh_3 to changes within the ligand sphere.

In detail one sees that there is very little difference between equivalent complexes of PCP and PCP-Ph or between complexes of NCN and NCN-Ph. For example, comparison of the $-PPh_2$ resonance position of PCP complex **1** at 36.5 ppm, with that of PCP-Ph complex **2** at 36.7 ppm shows that the introduction of a phenyl group *para* to the C_{ipso}−Ru bond affords only a modest deshielding of +0.2 ppm; for the PPh_3 resonances in the same complexes the effect of the phenyl group is to decrease the deshielding by 0.5 ppm. However, the influence of the auxiliary ligands is more dramatic.

(19) Valk, J.-M.; van Belzen, R.; Boersma, J.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Dalton Trans.* **1994**, 2293.

(20) (a) Alsters, P. L.; Engel, P. F.; Hogerheide, M. P.; Copijn, M.; Spek, A. L.; van Koten, G. *Organometallics* **1993**, *12*, 1831. (b) Markies, B. A.; Wijkens, P.; Kooijman, H.; Spek, A. L.; Boersma, J.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1992**, 1420.

When the Cl^- ligand in **1** is replaced by triflate anion (a weaker σ-donor) to afford **3**, the shift for the PPh_3 resonances decreases 5.4 ppm from 81.3 to 75.9 ppm; the effect on the PPh_2 resonances is more modest and affords, in contrast, a shift increase of 1.7 ppm. The replacement of the donor ligands PPh_3 and Cl^- in neutral complex **2** for the strongly π-accepting terpy in cationic complex **6** results in a shift of the $-PPh_2$ resonance from 36.7 to 42.5 ppm. This increased deshielding of 5.8 ppm reflects clearly the different nature and coordination of these two species.

The ^{31}P NMR resonance for the PPh_3 ligand in PCP-R-4 complexes is found some 9−12 ppm to upfield of the corresponding resonance in analogous NCN-R-4 complexes. This result cannot be explained by the expected donor characteristics of the heteroatoms in these ligands, and an explanation has to be sought in the relative steric constraints in these complexes and their effects on the metal coordination sphere. Since the determined cone angle of PPh_3 is 145° [21] and of NMe_3 is 132° [22] (so giving an idea of the difference to be expected for related $R-PPh_2$ and $R-NMe_2$ groups), one might anticipate that steric congestion in the ruthenium PCP-R-4 complexes would be more severe than in the NCN-R-4 analogs. However, molecular modeling[23] shows that as a consequence of the larger atomic radius of phosphorus compared to nitrogen and of the lower steric bulk of the slim flat phenyl groups compared to the spherical and rigidly positioned *N*-methyl groups it is the NCN-R-4 species that are more crowded. These differences are primarily reflected in the relative positions of the chloro atom with respect to the apical phosphorus atom with the NCN analog having the most pronounced square-pyramidal structure. It is interesting to see that ^{13}C NMR data for C_{ipso} in analogous ruthenium PCP-R-4 and NCN-R-4 complexes (Table 1) also show trends that run contrary to electron-donating properties of these two ligands. Unexpectedly, it is the NCN-R-4 ligands that provide the higher C_{ipso} chemical shifts in combination with smaller ^2J(CP) values. In ongoing studies we are investigating further the significance of these NMR data/structure correlations.[10b]

Chemical Aspects of PCP-R-4 and NCN-R-4 Complexes. From a chemical point of view, one of the noticeable features of the PCP complex **1** (and other PCP-R-4 complexes reported here) is the much lower sensitivity toward oxidation by O_2 than its NCN analog. This is understandable since, compared to a $-PPh_2$ group, the $-NMe_2$ group with its purely electron-donating character (*vide supra*) will give rise to a higher electron density on the Ru(II) center and, therefore, to a lower redox potential. At the same time a higher oxidation state of the metal, e.g. Ru(III), is more stabilized by coordination of the hard nitrogen donor site.[11,24]

The electronic differences between PCP and NCN complexes are also seen in the ability of an auxiliary metal-bound ligand to function as a leaving group. Whereas the very weakly coordinating ligand OTf^- in **3** is replaced readily by the better donor I^-, the reactions of the five-coordinate PCP complexes **1** and **2** with KI are relatively slow. Since exchange of the chloride in $[RuCl(NCN)(PPh_3)]$ for iodide is fast at room temperature,[10a] the reluctance of Cl^- to be exchanged for I^- in PCP complexes **1** and **2** can be interpreted as being due to the electron-accepting character of the PPh_2 groups that in a dissociative mechanism leads to destabilization of the intermediate cation $[Ru(PCP)(PPh_3)]^+$. The influence of the leaving group X on the reactivity of 16-electron complexes $[RuX(PCP\text{-}R\text{-}4)(PPh_3)]$ (X = Cl, **1** and **2**; X = OTf, **3**; I, **4**) was also demonstrated in their reactions with the terdentate *N*,*N*′,*N*″-donor ligand terpy. On the one hand, to form ionic complex **6** from chloro complex **2** strenuous reaction conditions over a prolonged time were required with significant amounts of byproducts, probably due to cyclometalation of a terpy ring, being generated. On the other hand, the presence of a better leaving group (OTf^-) in the starting material **3** led to fast coordination of the three N-donor atoms of terpy to afford ionic complex **5** while no side products were formed. We ascribe the fact that PCP-Ph complex **2** does react with terpy, whereas PCP complex **1** does not, to the weak electron-donating character of the phenyl group *para* to the $C_{ipso}-Ru$ bond in complex **2** that makes the chloride anion a better leaving group. A similar effect was not observed for NCN-R-4 complexes $[RuCl(NCN\text{-}R\text{-}4)(PPh_3)]$(R = H, Ph), where the halide is expected to be much less strongly bound than in the PCP-R-4 analogs, and terpy readily replaces the PPh_3 and Cl^- ligands in such complexes to give the corresponding cationic terpy species.[10]

Summary

With the monoanionic $[C_6H_2(CH_2PPh_2)_2\text{-}2,6\text{-}R\text{-}4]^-$ ligand, PCP-R-4, it has been possible to prepare complexes of the type $[RuX(PCP\text{-}R)(PPh_3)]$ in which a 16-electron ruthenium(II) center is stabilized. These new complexes allow structural and chemical parallels to be drawn with analogous complexes containing aryldiamine ligands $[C_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}R\text{-}4]^-$, NCN-R-4. As in the NCN-R-4 complexes, the PCP-R-4 system is bound in a *pseudo*meridional manner to ruthenium and a square-pyramidal overall geometry is usual. The main differences in reactivity found between PCP-R-4 and NCN-R-4 complexes are due to the enhanced acceptor character and the decreased steric demand of $-PPh_2$ groups compared to $-NMe_2$ groups. The PCP-R-4 complexes are thermally stable arylruthenium(II) species, some of which show fluxional behavior in solution, in which the $C_{ipso}-Ru$ σ-bond is remarkably robust and is, for example, inert to reagents such as boiling methanol. The triflate complex $[Ru(OTf)(PCP)(PPh_3)]$, **3**, for which the NCN analog is unknown, has recently allowed entry into chemistry which includes an interesting, but as yet not fully characterized, species that probably contains one monoanionic PCP ligand and one neutral PC(H)P ligand.[25]

Experimental Section

The complexes $[RuCl_2(PPh_3)_4]$[14] and $[RuCl(NCN\text{-}R\text{-}4)(PPh_3)]$[10] and the diphosphine 1,3-bis[(diphenylphosphino)methyl]ben-

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(22) Seligson, A. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1991**, *113*, 89.
(23) CAChe scientific software, using augmented MM2 parameters.
(24) (a) Beley, M.; Collin, J.-P.; Louis, B.; Metz, J. P.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 8521−8522. (b) Beley, M.; Collin, J.-P.; Sauvage, J.-P. *Inorg. Chem.* **1991**, *113*, 8521.
(25) Dani, P.; Karlen, T.; Grove, D. M.; Spek, A. L.; Smeets, W. J. J.; van Koten, G. Manuscript in preparation.

zene, PC(H)P,[2] were prepared as described in the literature. Purchased chemicals were used without further purification. Solvents were dried by standard procedures and stored under nitrogen. All manipulations were carried out using Schlenk techniques in a dry nitrogen atmosphere, unless stated otherwise. Elemental analyses were performed by Dornis und Kolbe, Mikroanalytisches Laboratorium (Mülheim, Germany). NMR spectra were recorded on a Bruker AC-200 or Bruker AC-300 spectrometer; ^{13}C and ^{31}P NMR spectra were recorded with broadband proton decoupling at 300 K unless stated otherwise. For NMR data, the following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet; t_{ap}, apparent triplet; td, triplet of doublets; br, broad.

Synthesis of 1-Phenyl-3,5-dimethylbenzene, C_6H_3-Ph-1-Me_2-3,5. A solution of phenyl boronic acid (33.4 g, 184 mmol) in MeOH (80 mL) was added dropwise to a vigorously stirred mixture of 2 M aqueous Na_2CO_3 (150 mL) and toluene (300 mL), containing 1-bromo-3,5-dimethylbenzene (25 g, 135 mmol). [$Pd(PPh_3)_4$] (1 g, 0.87 mmol) was added, and the mixture was stirred for 3 days. Addition of CH_2Cl_2 (500 mL) and 2 M aqueous Na_2CO_3 (800 mL) containing concentrated ammonia (100 mL) resulted in partitioning of the mixture. The separated organic layer was washed with saturated brine (150 mL) and dried over $MgSO_4$, and the volatilies were removed *in vacuo*. The crude product was purified by flash distillation to give a colorless oil, bp 84−86 °C/0.6 mmHg (lit.: 155 °C/16 mmHg).[26] Yield: 23.3 g, 95%. MS (EI, 70 eV): *m*/*z* (rel intensity) 182 (M^+, 100%), 167 (58.2), 152 (13.1), 89 (11.5), 76 (12.2). ^1H NMR (200.13 MHz, $CDCl_3$): δ 2.45 (s, 6 H, CH_3), 7.1−7.8 (m, 8 H, aromatic). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 21.76, 125.5, 127.44, 127.56, 129.02, 129.28, 138.52, 141.65, 141.87. n_D^{20}: 1.5949 (lit.: 1.5952).[27]

Synthesis of 1-Phenyl-3,5-bis(bromomethyl)benzene, C_6H_3-Ph-1-$(CH_2Br)_2$-3,5. To a solution of C_6H_3-Ph-1-Me_2-3,5 (25.5 g, 0.14 mol) in dry CCl_4 (300 mL) were added *N*-bromosuccinimide (47.88 g, 0.269 mol) and 2,2′-azobis(isobutyronitrile), AIBN (0.5 g). The mixture was heated at gentle reflux until vigorous boiling indicated the start of the reaction, and stirring without further heating was continued until boiling ceased. The resulting mixture was then heated at reflux for 12 h. The solution was cooled to room temperature and filtered and the filtrate collected. The solid residue was extracted with CCl_4 (100 mL), and the filtrate and extract were combined. Evaporation of this solution to dryness on a rotary evaporator afforded the crude product. Pure white crystalline product was obtained by two subsequent crystallizations from hexanes. Yield: 17.1 g, 36%. MS (EI, 70 eV): *m*/*z* (rel intensity) 342, 340, 338 (M^+, 4.1, 8.2, 4.1%), 261, 259 (90.1), 180 (100), 165 (41.5), 89 (51.4), 63 (22.4). ^1H NMR (200.13 MHz, $CDCl_3$): δ 4.54 (s, 4 H, CH_2), 7.26−7.6 (m, 8 H, aromatic). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 32.86, 127.18, 127.89, 127.95, 128.35, 128.91, 138.91, 139.89, 147.21.

Synthesis of 1-Phenyl-3,5-bis[(diphenylphosphino)-methyl]benzene, C_6H_3-Ph-1-$(CH_2PPh_2)_2$-3,5, PC(H)P-Ph. Sodium (1.28 g, 55.7 mmol), PPh_3 (7.3 g, 27.9 mmol), and NH_4-Br (2.7 g, 27.6 mmol) were sequentially added to liquid ammonia (200 mL) at −78 °C at intervals of 30 min. To this solution was added C_6H_3-Ph-1-$(CH_2Br)_2$-3,5 (4.6 g, 13.8 mmol) as a slurry in dry Et_2O. The resulting mixture was stirred for 6 h at −78 °C, after which the external cooling was removed and the solvents were allowed to evaporate in a stream of nitrogen overnight. The residue was washed twice with water, once with MeOH, and twice with hexane. The resulting white solid product was recrystallized from CH_2Cl_2/Et_2O. Yield: 5.84 g, 77% (mp 152−153 °C). ^1H NMR (200.13 MHz, CD_2Cl_2): δ 3.3−3.43 (s, 4 H, CH_2), 6.8−7.5 (m, 28 H, aromatic). ^{31}P NMR (80.96 MHz, CD_2Cl_2): δ −9.2 (s). Anal. Calcd for $C_{38}H_{32}P_2$: C, 82.92; H, 5.81. Found: C, 83.10; H, 5.81.

Synthesis of (2,6-Bis[(diphenylphosphino)methyl]-phenyl)chloro(triphenylphosphine)ruthenium(II), [Ru^{II}-Cl{$C_6H_3(CH_2PPh_2)_2$-2,6}(PPh_3)], 1. A solution of PC(H)P (500 mg, 1.1 mmol) in CH_2Cl_2 (10 mL) was added to [$RuCl_2(PPh_3)_4$] (1.2 g, 1.0 mmol) in CH_2Cl_2 (30 mL). The mixture was heated at reflux for 3 days, concentrated to 5 mL, and then layered with pentane (30 mL). Upon agitation, a green powder precipitated from solution. The solid was filtered off, washed with pentane, and dried *in vacuo*. Yield: 0.51 g, 58% (mp >200 °C). ^1H NMR (200.13 MHz, CD_2Cl_2): δ 2.53 (td br, ^2J(HH) 15.9 Hz, $|^2J(HP) + {}^4J(HP)|$ not resolved, 2 H, CH_2), 3.49 (td, ^2J(HP) 15.9 Hz, $|^2J(HP) + {}^4J(HP)|$ 6 Hz, 2 H, CH_2), 6.7−8.3 (m, 38 H, aromatic). ^{31}P NMR (80.96 MHz, CD_2Cl_2): δ 36.5 (d, ^2J(PP) 31.7 Hz, PPh_2), 81.3 (t, ^2J(PP) 31.7 Hz, PPh_3). ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ 40.77 (t_{ap}, *J*(CP) 15 Hz, CH_2), 123.6−138.7 (13 resonances: 5 s, 2 d, 4 t, 2 m), 151.8 (t_{ap}, *J*(CP) 8.7 Hz), 172.7 (d, ^2J(CP) 16.6 Hz, C_{ipso}). Anal. Calcd for $C_{50}H_{42}ClP_3Ru + 0.5\ CH_2Cl_2$: C, 66.33; H, 4.81. Found: C, 66.45; H, 5.05.

Synthesis of (4-Phenyl-2,6-bis[(diphenylphosphino)-methyl]phenyl)chloro(triphenylphosphine)ruthenium-(II), [Ru^{II}Cl{$C_6H_2(CH_2PPh_2)_2$-2,6-Ph-4}(PPh_3)], 2. A solution of PC(H)P-Ph (0.8 g, 1.45 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a stirred solution of [$RuCl_2(PPh_3)_4$] (1.65 g, 1.35 mmol) in CH_2Cl_2 (20 mL) at room temperature. The mixture was heated at reflux for 15 h and subsequently concentrated to 5 mL. Upon addition of Et_2O/pentane dark green microcrystals formed, which were filtered off and washed with pentane followed by drying *in vacuo*. Yield: 1.0 g, 78% (mp >200 °C). ^1H NMR (300.13 MHz, CD_2Cl_2): δ 2.5 (td br, ^2J(HP) 16.1 Hz, $|^2J(HP) + {}^4J(HP)|$ not resolved, 2 H, CH_2), 3.57 (td, ^2J(HP) 16.1 Hz, $|^2J(HP) + {}^4J(HP)|$ 6 Hz, 2 H, CH_2), 6.8−8.0 (m, 42 H, aromatic). ^{31} P NMR (80.96 MHz, CD_2Cl_2): δ 36.7 (d, ^2J(PP) 31.8 Hz, PPh_2), 80.8 (t, ^2J(PP) 31.8 Hz, PPh_3). ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ 39.1 (t_{ap}, *J*(CP) 15.3 Hz, CH_2), 121−142 (13 resonances: 5 s, 2 d, 4 t, 2 m), 151.3 (t, *J*(CP) 8.6 Hz), 173.2 (d, *J*(CP) 17.3 Hz, C_{ipso}). Anal. Calcd for $C_{56}H_{46}ClP_3Ru$: C, 70.94; H, 4.85. Found: C, 70.76; H, 4.94.

Synthesis of (2,6-Bis[(diphenylphosphino)methyl]-phenyl)trifluoromethanesulfonato(triphenylphosphine)-ruthenium(II), [$Ru^{II}(OSO_2CF_3)$){$C_6H_3(CH_2PPh_2)_2$-2,6}-(PPh_3)], 3. AgOTf (166 mg, 0.65 mmol) was added to a stirred solution of **1** (500 mg, 0.57 mmol) in CH_2Cl_2 (20 mL). After 3 h of stirring at room temperature under exclusion of light, the green solution was separated from the formed white precipitate by centrifugation. The solution was evaporated to dryness, and the residue was extracted with benzene (30 mL). After removal of the benzene, the residue was dissolved 10 mL of CH_2Cl_2. Addition of pentane resulted in the formation of a green powder, which was collected and washed twice with hexane (20 mL) and dried *in vacuo*. Yield: 300 mg, 53% (mp 172 °C (dec)). ^1H NMR (200.13 MHz, CD_2Cl_2): δ 2.31−2.49 (td br, ^2J(HH) 16.5 Hz, $|^2J(HP) + {}^4J(HP)|$ not resolved, 2 H, CH_2), 3.32−3.49 (td, ^2J(HH) 16.5 Hz, $|^2J(HP) + {}^4J(HP)|$ 6.4 Hz, 2 H, CH_2), 6.68−8.09 (m, 23 H, aromatic). ^{31}P NMR (80.96 MHz, CD_2Cl_2, 220 K): δ 38.2 (d, ^2J(PP) 31.7 Hz, PPh_2), 75.9 (t, ^2J(PP) 31.7 Hz, PPh_3). ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ 37.5 (t_{ap}, *J*(CP) 15.1 Hz, CH_2), 122−136 (11 resonances: 4 s, 2 d, 3 t, 2 m), 163.5 (t_{ap}, *J*(CP) 9.3 Hz), 164.6 (d, ^2J(CP) 17.0 Hz, C_{ipso}). Anal. Calcd for $C_{51}H_{42}F_3P_3O_3SRu + 0.75\ CH_2Cl_2$: C, 59.23; H, 4.15. Found: C, 59.20; H, 4.01.

Synthesis of (2,6-Bis[(diphenylphosphino)methyl]-phenyl)iodo(triphenylphosphine)ruthenium(II), [Ru^{II}I{$C_6H_3(CH_2PPh_2)_2$-2,6}(PPh_3)], 4. A solution of **1** (500 mg, 0.57 mmol) in MeOH (10 mL) containing an excess of KI (3 g, 18 mmol) was heated at reflux for 4 days. After removal of the solvent *in vacuo*, the residue was extracted once with C_6H_6 (20 mL) followed by separation from insoluble material by centrifugation. After concentration of the resulting green solution to 5 mL, a green powder was precipitated by addition of hexane. The solid was filtered off, washed twice with pentane, and dried *in vacuo*. Yield: 0.30 g, 64% (mp > 200 °C). ^1H NMR (200.13 MHz, CD_2Cl_2): δ 2.59 (td br, ^2J(HH) 16.0 Hz, $|^2J(HP) + {}^4J(HP)|$ not resolved, 2 H, CH_2), 3.54 (td, ^2J(HP)

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(27) Johnson, E. A. *J. Chem. Soc. London* **1957**, 4155.

16.0 Hz, $|^2J(HP) + {}^4J(HP)|$ 6 Hz, 2 H, CH_2), 6.7−8.1 (m, 38 H, aromatic). ^{31}P NMR (80.96 MHz, CD_2Cl_2): δ 36.2 (d, $^2J(PP)$ 32.4 Hz, PPh_2), 77.2 (t, $^2J(PP)$ 32.4 Hz, PPh_3). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 40.5 (t_{ap}, $J(CP)$ 14.6 Hz, CH_2), 122−137 (14 resonances: 2 s, 2 d, 5 t, 5 m), 150.57 (t_{ap} $J(CP)$ 8.5 Hz), 177.3 (d, $^2J(CP)$ 16.0 Hz, C_{ipso}). Anal. Calcd for $C_{50}H_{42}ClP_3Ru$: C, 62.33; H, 4.38. Found: C, 62.38; H, 4.64.

Alternative Synthesis of 4 Using the Triflate Complex 3. A solution of complex **3** in MeOH with an equimolar amount of KI was stirred for 3 h at room temperature. Workup as described above afforded **4** in 85% yield.

Synthesis of (4-Phenyl-2,6-bis[(diphenylphosphino)-methyl]phenyl)(2,2′:6′,2″-terpyridine)ruthenium(II) Chloride, [Ru^{II}{$C_6H_2(CH_2PPh_2)_2$-2,6-Ph-4}(terpy)]Cl, 5. A solution of terpy (50 mg, 0.214 mmol) in MeOH (10 mL) was added to a solution of **2** (200 mg, 0.211 mmol) in MeOH (10 mL). The mixture was heated at reflux for 3 days. During this time, the color changed slowly from green to red. The solvent was removed *in vacuo*, and the residue was extracted with CH_2Cl_2 (10 mL). Addition of pentane/Et_2O resulted in precipitation of an air-stable red powder, which was collected, washed with Et_2O, and dried *in vacuo*. Yield: 0.104 g, 54% (mp 175 °C). ^1H NMR (200.13 MHz, CD_2Cl_2): δ 3.95 (s, 4 H, CH_2), 6.3−9.1 (m, 38 H, aromatic). ^{31}P NMR (80.96 MHz, CD_2Cl_2): δ 42.5 (s). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 41.73 (t_{ap}, $J(CP)$ 16.8 Hz, CH_2), 120.25 (t_{ap}, $J(CP)$ 8.4 Hz), 123.2 (s), 123.7 (s), 125.92 (s), 126.41 (s), 126.57 (s), 128.33 (t_{ap}, $J(CP)$ 4.2 Hz), 128.89 (s), 129.26 (s), 129.92 (t_{ap}, $J(CP)$ 5.2 Hz), 132.3 (t_{ap}, $J(CP)$ 17.3 Hz), 134.4 (s), 135.0 (s), 135.96 (s), 141.58 (s), 147.45 (t_{ap}, $J(CP)$ 9.4 Hz), 152.09 (s), 154.31 (s), 157.53 (s), 182.20 (t_{ap}, $J(CP)$ 6.5 Hz), 183.5 (s, C_{ipso}). Anal. Calcd for $C_{53}H_{42}ClN_3P_2Ru$: C, 69.26; H, 4.57; N, 4.57. Found: C, 68.98; H, 4.68; N, 4.53.

Synthesis of (2,6-Bis[(diphenylphosphino)methyl]-phenyl)(2,2′:6′,2″-terpyridine)ruthenium(II) Trifluoromethanesulfonate, [Ru^{II}{$C_6H_3(CH_2PPh_2)_2$-2,6}(terpy)]OTf, 6. The air-stable, red complex **6** was synthesized as described for **5** by heating the triflate complex **3** and 1 equiv of terpy in MeOH at reflux for 3 h. Yield: 68% (mp 127 °C (dec)). ^1H NMR (200.13 MHz, CD_2Cl_2): δ 3.95 (t_{ap}, 4 H, $J(HP)$ 3 Hz, CH_2), 6.4−8.8 (m, 34 H, aromatic). ^{31}P NMR (80.96 MHz, CD_2Cl_2): δ 42.7 (s). ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ 43.4 (t_{ap}, $J(CP)$ 17.2 Hz, CH_2), 124.0 (m), 126.6 (s) 125.3 (s), 128.3 (s), 130.3 (t_{ap}, $J(CP)$ 4.1 Hz), 131.2 (s), 131.9 (t, $J(CP)$ 5.3 Hz), 134.5 (t, $J(CP)$ 17.3 Hz), 135.3 (s), 136.6 (s), 148.9 (t_{ap}, $J(CP)$ 10.1 Hz), 154.5 (s), 156.5 (s), 159.2 (s), 182.3 (s, C_{ipso}). Anal. Calcd for $C_{48}H_{38}F_3N_3P_2O_3SRu$: C, 60.26; H, 3.97. Found: C, 59.95; H, 4.11.

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