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Ligand Sphere Conversions in Terminal Carbide Complexes

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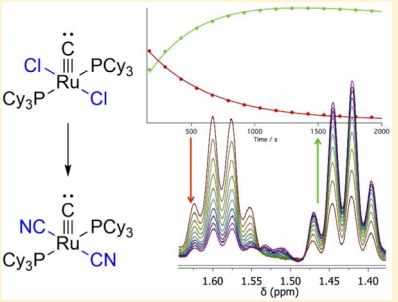
Supporting Information

ABSTRACT: Metathesis is introduced as a preparative route to terminal carbide complexes. The chloride ligands of the terminal carbide complex $[RuC(Cl)_2(PCy_3)_2]$ (**RuC**) can be exchanged, paving the way for a systematic variation of the ligand sphere. A series of substituted complexes, including the first example of a cationic terminal carbide complex, $[RuC(Cl)(CH_3CN)(PCy_3)_2]^+$, is described and characterized by NMR, MS, X-ray crystallography, and computational studies. The experimentally observed irregular variation of the carbide ^{13}C chemical shift is shown to be accurately reproduced by DFT, which also demonstrates that details of the coordination geometry affect the carbide chemical shift equally as much as variations in the nature of the auxiliary ligands. Furthermore, the kinetics of formation of the sqaure pyramidal dicyano complex, *trans*-$[RuC(CN)_2(PCy_3)_2]$, from **RuC** has been examined and the reaction found to be quite sluggish and of first order in both **RuC** and cyanide with a rate constant of $k = 0.0104(6)$ m^{-1} s^{-1}. Further reaction with cyanide leads to loss of the carbide ligand and formation of *trans*-$[Ru(CN)_4(PCy_3)_2]^{2-}$, which was isolated and structurally characterized as its PPh_4^+ salt.



INTRODUCTION

The chemistry of molecular carbides is currently in rapid development. In fuel synthesis by the Fischer−Tropsch process,[1] carbide ligands on catalyst surfaces are possibly key intermediates, entering C−C bond forming steps.[2] Additionally, the remarkable report of a central interstitial carbide ligand in the FeMo-cofactor of nitrogenase[3] suggests that carbide ligands may tune catalytic properties. Metal complexes with terminal carbide ligands (groups 6 and 8)[4−10] are relatively rare compared with complexes with other monatomic terminal ligands such as fluoride, oxide, or nitride. In contrast to the situation for oxide[11] and nitride[12,13] complexes, no preparative routes to carbide complexes involving atom-transfer reactions have been found. Thus, only two strategies for forming terminal carbide complexes exist. Cleaving of carbon-derived ligands provides by far the most explored route to terminal carbide complexes.[4−10] The second strategy of auxiliary ligand sphere modification provides a simple, though virtually unexplored, approach.[10]

As might be anticipated, most reported chemistry of terminal carbide systems engages the carbide ligand of the M≡C: unit. These reactions cover functionalization with nonmetals to incorporate the carbon atom into larger organometallic fragments[4,8−10,14,15] and bridge formation with transition metal fragments to afford heterometallic carbide-bridged complexes.[7,16] Similarly, carbide ligands coordinated to main group metals, M≡C−M′, are prone to react like their terminal congeners thus participating in relay-like reactions where transition metal or other main group fragments replace the main group metal fragments at the carbide ligands.[17] Contrary to complexes with terminal nitride ligands [VN],[18] [CrN],[13,19] [MoN],[20] [WN],[21] [MnN],[22] [TcN],[23] [ReN],[24] [RuN],[25] and [OsN],[26] or bridging carbide ligands,[27] substitution reactions in the peripheral ligand sphere of terminal carbide complexes have barely been investigated. The only experimental report of such reactivity is Johnson's description that $[OsC(Cl)_2(PCy_3)_2]$ exchanges its chloride ligands for iodide upon reaction with Me_3SiI. However, computational studies[28] suggest variation of the ligand sphere to be a powerful entry to manipulation of the stability and electronic properties of terminal carbide moieties. Consequently, we have investigated the feasibility of ligand substitution in the terminal carbide $[RuC(Cl)_2(PCy_3)_2]$ (**RuC**). This, remarkably stable carbide complex was first synthesized by Heppert[6] and further investigated by Grubbs[7] and Johnson.[9,29] Here, it will be demonstrated, that despite the robust nature of **RuC**, ligand substitutions which preserve the terminal carbide ligand are feasible and provide a useful approach to systematic modifications of the environment of the terminal carbide ligand.

RESULTS AND DISCUSSION

Reaction of a chloroform solution of **RuC** with a suitable cyanide salt, e.g., $(Ph_4P)CN$, results in ligand exchange and the formation of $[RuC(CN)_2(PCy_3)_2]$, (**RuC-(CN)$_2$**) (see Scheme 1). The exchange is relatively slow (vide infra), and with a 2−3 fold excess of cyanide, the reaction is complete after 30 min as shown by ^{13}C NMR, during which time the color changes from yellow to almost colorless. The complex decomposes relatively fast in the chloroform solution mixture, hampering its isolation. However, when the reaction is performed in dichloromethane, the solution is comparatively stable, and upon concentration, it precipitates an off-white powder that can be recrystallized from boiling acetonitrile. The reaction between **RuC** and cyanide to

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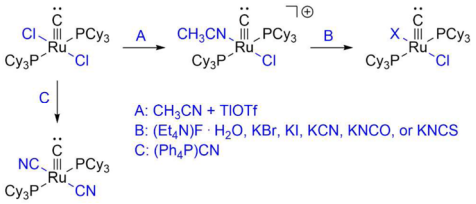
Scheme 1. Synthetic Routes to RuC-$(CN)_2$ and Mono-Substituted Species, RuC-X



form **RuC-$(CN)_2$** relies on the ready association of cyanide with ruthenium. In contrast to this, fluoride, bromide, iodide, azide, cyanate, and thiocyanate fail to substitute the chloride ligands directly. However, chloride abstraction, using Tl^+ in acetonitrile, affords the monosubstituted cationic $[RuC(Cl)(MeCN)(PCy_3)_2]^+$, **RuC-MeCN**. Mass spectra of **RuC-MeCN** reveal cations with m/z = 750.38 and 709.35 corresponding to **RuC-MeCN** and its acetonitrile-deprived derivative, suggesting weak coordination of MeCN. The conversions capitalize on this aspect, as the cationic terminal carbide complex readily traps halides and pseudohalides ($X = F^-$, Br^-, I^-, CN^-, NCO^-, and NCS^-) to form $[RuC(Cl)(X)(PCy_3)_2]$ (**RuC-X**), thus enabling the isolation of systematically modified terminal carbide complexes.

X-ray crystal structures were obtained for the compounds **RuC-$(CN)_2$**, **RuC-MeCN**, **RuC-NCO**, **RuC-CN**, and **RuC-Br**. Thermal ellipsoid plots of the first two are given in Figure 1 and

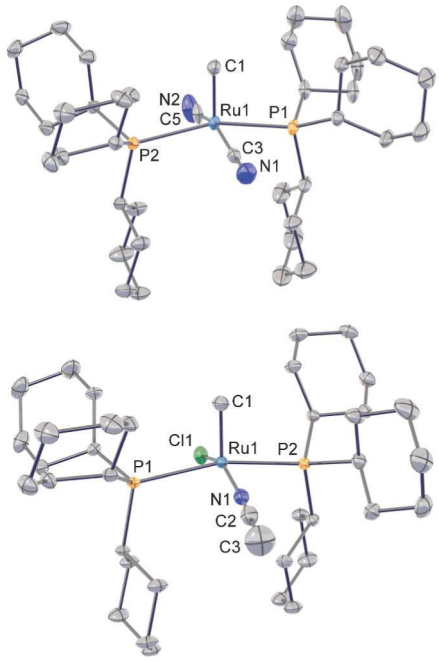


Figure 1. Thermal ellipsoid plots of **RuC-$(CN)_2$** (top) and the complex cation of **RuC-MeCN** (bottom) shown at 50% probability and with hydrogen atoms omitted.

the remaining, structurally similar examples are shown in the Figure S1. The ruthenium-carbide distances vary only a little in the complexes falling in the range 1.636(3)−1.645(2) Å. For **RuC-$(CN)_2$**, Ru-CN distances are 2.071(3) and 2.076(3) Å, slightly longer than the average Ru-CN distance (2.01(5) Å) for structures in the CSD. The C−Ru−CN angles are 99.20(13) and 99.36(15)°, which is smaller than the C−Ru−Cl angle of 102.8° for **RuC**. A similar trend is observed in **RuC-MeCN** where the C−Ru−Cl angle is 103.20(7)°, and the C−Ru−N angle is 97.41(8)°. Cyanide and acetonitrile are π-backbonding ligands, and optimal overlap for backbonding requires the C−Ru−L angle to be close to 90°, which might explain the smaller angles for these ligands compared to that of chloride.

^{13}C NMR is convenient for monitoring reactions with **RuC** due to the ease of ^{13}C-labeling of the carbide ligand using ^{13}C-labeled vinyl acetate. The characteristic high chemical shifts for the terminal carbide (>450 ppm) make it easy to identify changes in the environment around the carbide. Table 1 lists chemical shifts of **RuC** as well as of the new terminal carbide complexes synthesized in this study.

Table 1. $[RuC(X)(Y)(PR_3)_2]$ Carbide ^{13}C Resonances in Chloroform (R = Cy) and Calculated for Model Systems (R = Me)

compound	experimental shift R = Cy/ppm	calculated shift R = Me/ppm
$[RuC(PR_3)_2Cl_2]$, **RuC**	471.7	470
$[RuC(PR_3)_2(CN)_2]$, **RuC-$(CN)_2$**	464.7	467
$[RuC(PR_3)_2ClF]$, **RuC-F**	473.4	474
$[RuC(PR_3)_2ClBr]$, **RuC-Br**	471.4	466
$[RuC(PR_3)_2ClI]$, **RuC-I**	469.7	463
$[RuC(PR_3)_2Cl(CN)]$, **RuC-CN**	474.9	476
$[RuC(PR_3)_2Cl(\underline{N}CO)]$, **RuC-NCO**	473.5/474.7	480
$[RuC(PR_3)_2Cl(\underline{O}CN)]$, **RuC-NCO**	473.5/474.7	485
$[RuC(PR_3)_2Cl(NCS)]$, **RuC-NCS**	477.5	484
$[RuC(PR_3)_2Cl(NCCH_3)]^+$, **RuC-MeCN**	485.7	493

In the **RuC-X** series where X = F, Cl, Br, and I, the carbide resonances change as would be expected based on the electronegativity of X, namely, from relatively deshielded carbide resonances in **RuC-F** to relatively shielded carbide resonances in **RuC-I**. An irregular trend is observed in the cyanide-substituted species. Exchanging one chloride in **RuC** (471.7 ppm) for cyanide to give **RuC−CN** yields a more deshielded carbide (474.9 ppm), but exchanging both chlorides for cyanides to give **RuC-$(CN)_2$** yields a *less* deshielded carbide (464.7 ppm). This clearly demonstrates the difficulty in simplistic interpretation of carbide resonance positions in terms of molecular composition.

To elucidate the variations in δ_C, a DFT study was performed to dissect the variation in the chemical shifts of the carbide ligands. A DFT approach with geometry optimized structure models with PMe_3 emulating PCy_3, the PBE0 functional, and ZORA treatment of relativistic effects (cf. SI for more details of the computations) yielded calculated shifts in remarkable agreement with experiment, both qualitatively and quantitatively (cf. Table 1). Numerical values are correct within 9 ppm, often better, and trends within substitution series are reproduced, including the upfield shift of the carbide resonances in **RuC-X** when X changes to heavier halides, as well as the aforementioned puzzling trend in the **RuC**/**RuC−CN**/**RuC-$(CN)_2$** series. The origin of this irregular variation was investigated further. The ruthenium−carbide distances are nearly constant for the systems (vide supra), and thus, the most

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obvious geometrical difference lies in the C−Ru−L angles. The angular variation is reproduced in the geometry optimized model systems, and importantly, for the **RuC−CN** model, the C−Ru−Cl angle is larger than the C−Ru−CN angle, thus mirroring the crystal structures. To investigate the angular dependence of the chemical shifts, we evaluated δ_C for the **RuC** model $[RuC(Cl)_2(PMe_3)_2]$ with the bond angles for **RuC-(CN)$_2$** and vice versa. These calculations suggested that two competing effects produce the observed chemical shifts. For the chloride/cyanide ligand systems, the effect of the different geometries and the nature of the ligand are of the same magnitude (both on the order of 25 ppm) but with opposite signs, thereby almost canceling out, and the observed trend is therefore the result of this tug of war (see SI for details). Table 2 contains experimental and calculated coupling constants, and

Table 2. Experimental and Calculated NMR Parameters for RuC and RuC-(CN)$_2$ and Their Model Systems

compound	δ_C (carbide) (ppm)	δ_C (cyanide) (ppm)	$^2J_{C-P}$ (Hz)	$^2J_{C-CN}$ (Hz)	$^2J_{P-CN}$ (Hz)
$[RuC(Cl)_2(PCy_3)_2]$, **RuC**	471.7		4.16		
$[RuC(Cl)_2(PMe_3)_2]$ (calc.)	471		−2.0		
$[RuC(CN)_2(PCy_3)_2]$, **RuC-(CN)$_2$**	464.7	136.7	not res.	not res.	13.7
$[RuC(CN)_2(PMe_3)_2]$ (calc.)	467	145	0.47	−0.64	17.4

in contrast to the well-resolved coupling to phosphorus in parent **RuC** (virtual t, $^2J_{C-P}$ = 4.16 Hz), the carbide resonance in **RuC-(CN)$_2$** appears as a singlet, also with ^{13}CN in the ligand sphere. However, the cyanide signal at 136.7 ppm is a triplet ($^2J_{C-P}$ = 13.7 Hz); these findings are also corroborated by the calculated magnitudes of the coupling constants in combination with the experimentally observed line widths.

The conversion of **RuC** with cyanide to afford **RuC-(CN)$_2$** is relatively slow and can be monitored by NMR (cf. Figure 2). Steady-state kinetics experiments with a > 20-fold excess of cyanide were performed for a range of cyanide concentrations, and a second order rate constant for the formation of **RuC-(CN)$_2$** in chloroform was determined to be k_2 = 0.0104(6) M^{-1} s^{-1} (see SI for details). The reaction is slow compared with substitution reactions involving the association of cyanide with phthalocyanine or porphyrin complexes of ruthenium[30] (k_2 = 0.052−41(1) $m^{-1}s^{-1}$).

The reaction is first order in cyanide, suggesting initial conversion of **RuC** to the apparently more reactive monosubstituted **RuC-CN**, which reacts rapidly to form **RuC-(CN)$_2$**. This enhanced reactivity is underlined by the absence of ^{1}H-resonances from **RuC-CN** in the reaction mixture. Moreover, mass spectra of **RuC-CN** in MeCN yield intense signals with m/z = 741.41 and 700.38, corresponding to $[RuC(CN)(MeCN)(PCy_3)_2]^+$ and $[RuC(CN)(PCy_3)_2]^+$, which suggests that the cyanide in **RuC-CN** labilizes the remaining chloride ligand. As mentioned, **RuC-(CN)$_2$** is unstable in the cyanide-containing chloroform solutions and decomposes over the course of 5−8 h depending on the cyanide concentration. A broad ^{13}C NMR signal at 121.9 ppm in chloroform suggests that excess cyanide reacts with the solvent to form the very strong acid $CH(CN)_3$ (pK_a = −5.0, anion $\delta_{C,\ CN}$ = 121.4).[31] After 5 days, excess cyanide has vanished, though a 20-fold excess was used. **RuC** is known to decompose in acidic solutions,[8,10,15] and **RuC-(CN)$_2$** parallels this instability. However, the decomposition product isolated here is not a carbene complex; rather, a relatively clean conversion into a ruthenium(II) complex *trans*-$[Ru(CN)_4(PCy_3)_2]^{2-}$ takes place. The ^{13}C NMR signal from the cyanide ligand is a triplet (160.2 ppm, $^2J_{C-P}$ = 13.1 Hz), and in

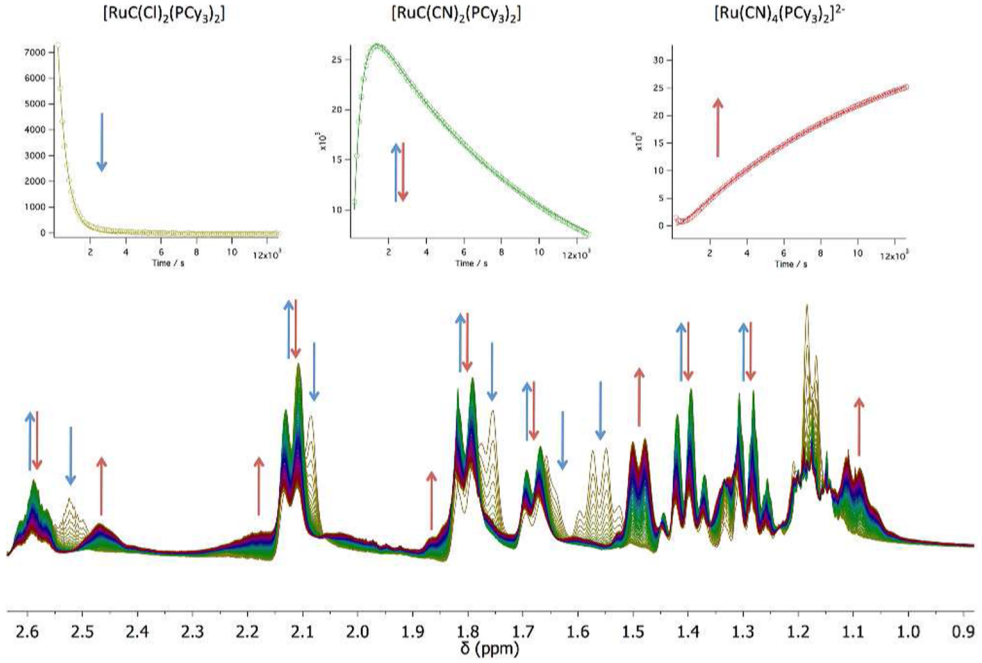

Figure 2. ^{1}H NMR spectra in the δ = 0.9−2.6 ppm region showing the reaction between **RuC** and cyanide in chloroform. Blue arrows indicate the first reaction where **RuC** is converted into **RuC-(CN)$_2$**, and red arrows indicate the second reaction where **RuC-(CN)$_2$** decomposes to *trans*-$[Ru(CN)_4(PCy_3)_2]^{2-}$. The top panels show fitted concentration curves for the three species.

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^{31}P NMR, a corresponding quintet (33.4 ppm, $^{2}J_{C-P}$ = 13.1 Hz) is observed with $^{13}CN^{-}$. The complex was isolated as the tetraphenylphosphonium salt and characterized by X-ray crystallography (cf. SI).

CONCLUSIONS

It is possible to vary the auxiliary ligands of the ruthenium carbide systematically by metathesis reactions, and in some ways, this is surprising in view of the sensitivity of synthetic routes to **RuC** toward the choice of phosphine ligands.[7] The chloride ligands are evidently not as critical for the stability of the RuC moiety as are the phosphine ligands, and even the cationic complex **RuC-MeCN** is quite stable. This particular complex with its labile acetonitrile ligand represents a convenient gateway to much more elaborately decorated terminal carbide systems for further studies.

In conclusion, we have demonstrated a facile and general route to a family of terminal ruthenium carbide complexes with varying auxiliary ligands. We have also demonstrated a computational approach, which accurately predicts the chemical shifts of such carbide species and elucidates the influence of the coordination geometry and nature of the auxiliary ligands on the chemical shift of the terminal carbide ligand.

EXPERIMENTAL SECTION

Syntheses. Unless otherwise stated, no attempts were made to exclude air in the syntheses. Chloroform (Sigma-Aldrich, HPLC, ≥ 99.8%), chloroform-*d* (Sigma-Aldrich, 99.8% D), dichloromethane (Sigma-Aldrich, HPLC, ≥ 99.8%), dichloromethane-d_2 (Sigma-Aldrich, 99.9% D), benzene-d_6 (Sigma-Aldrich, 99.6% D), acetonitrile (Riedel-de Haën, > 99.9%), diethyl ether (VWR Chemicals), tetraethylammonium fluoride hydrate (Sigma-Aldrich, 98%), and Silica Gel 60 Å (ROCC) were purchased from commercial suppliers and used as received. [Ru(C)Cl$_2$(PCy$_3$)$_2$] (**RuC**) and TlOTf were synthesized according to published procedures;[9,32] **Ru^{13}C** was obtained with $^{13}CH_2{}^{13}CHOAc$ (Sigma-Aldrich, 99% ^{13}C). (Ph$_4$P)CN was prepared by aqueous metathesis of sodium cyanide and tetraphenylphosphonium chloride and recrystallized from water.

Synthesis of [RuC(CN)$_2$(PCy$_3$)$_2$] (RuC-(CN)$_2$). **RuC** (35 mg (47 μmol)) and 100 mg (274 μmol) of (Ph$_4$P)CN were dissolved in 4 mL of dichloromethane and left for 3 h. In this time, the pale yellow solution turned almost colorless. The solution was evaporated to dryness (with N$_2$) and the crystalline precipitate thoroughly washed 3 times with methanol to remove excess (Ph$_4$P)CN and (Ph$_4$P)Cl formed in the reaction. The crude product was dissolved in 25 mL of boiling acetonitrile and left to evaporate to dryness yielding 16.3 mg of **RuC-(CN)$_2$**, 48% based on **RuC**. ^{1}H NMR, 500 MHz, CD_2Cl_2, δ: 2.69−2.59 (m, 6H), 2.24−2.13 (m, 12H), 1.93−1.83 (m, 12H), 1.80−1.71 (m, 6H), 1.53−1.41 (m, 12H), 1.41−1.30 (m, 12H), 1.30−1.22 (m, 6H). ^{13}C NMR, 126 MHz, CD_2Cl_2, δ: 465.23, 136.43 (t, $^{2}J_{C-P}$ = 13.6 Hz), 35.08 (virtual t, $^{1}J_{C-P}$ = 11.0 Hz), 30.68, 28.28 (virtual t, $^{1}J_{C-P}$ = 5.7 Hz), 26.99. ^{13}C NMR, 126 MHz, $CDCl_3$, δ: 464.75, 136.81 (t, $^{2}J_{C-P}$ = 13.5 Hz), 34.68 (virtual t, $^{1}J_{C-P}$ = 11.0 Hz), 30.24, 27.78 (virtual t, $^{1}J_{C-P}$ = 6.0 Hz), 26.51. ^{31}P NMR, CD_2Cl_2, δ: 49.65 (t, *J* = 13.6 Hz). Anal. Calcd for $C_{39}H_{66}N_2P_2Ru$: C 64.50%, H 9.17%, N 3.86%; found, C 64.14%, H 8.99%, N 3.84%.

Synthesis of [RuC(Cl)(MeCN)(PCy$_3$)$_2$]OTf (RuC-MeCN). Under a N$_2$ blanket, TlOTf (104.9 mg, 296.8 μmol) and **RuC** (105.0 mg, 141.0 μmol) were suspended in a mixture of 1 mL of chloroform and 1 mL of acetonitrile and heated to reflux temperature for 18 h. During this time, the solution changed color to dark green, and a white precipitate of TlCl formed. The solution was evaporated to dryness, and the residue extracted with dichloromethane (2 mL) and passed through a plug of silica (diameter 0.5 cm, length 4 cm) to absorb the dark green byproduct. The extract was evaporated to dryness, and the residue was dissolved in 2 mL of acetonitrile. After dilution with 50 mL of diethyl ether, the solution was left at 5 °C for 3 days. Pale yellow crystals of **RuC-MeCN** were separated from the mother liquor by decanting, washed with 15 mL of diethyl ether, and air-dried. Yield: 43.8 mg, 48.7 μmol, 34.5% based on **RuC**. Crystals suitable for X-ray crystallography were grown by this procedure. ^{1}H NMR, 500 MHz, CD_2Cl_2, δ: 2.80 (s, 3H), 2.52−2.39 (m, 6H), 2.20−2.13 (m, 6H), 2.13−2.07 (m, 6H), 1.97−1.87 (m, 12H), 1.82−1.75 (m, 6H), 1.72−1.60 (m, 6H), 1.53−1.41 (m, 6H), 1.39−1.24 (m, 18H). ^{13}C NMR, 126 MHz, $CDCl_3$, δ: 485.70, 137.87, 32.78 (virtual t, $^{1}J_{C-P}$ = 10.2 Hz), 30.46, 29.89, 28.03 (virtual t, $^{1}J_{C-P}$ = 5.1 Hz), 27.83 (t, *J* = 5.5 Hz), 26.47, 5.24. ^{31}P NMR, 202 MHz, CD_2Cl_2, δ: 43.37. ^{19}F NMR, 470 MHz, CD_2Cl_2, δ: − 78.93. ESI^{+} MS, CH_3CN, *m*/*z*, f/c: [RuC(Cl)(MeCN)(PCy$_3$)$_2$]$^{+}$: 750.38/750.36, [RuC(Cl)(PCy$_3$)$_2$]$^{+}$: 709.35/709.34. Anal. Calcd for $C_{40}H_{69}ClF_3NO_3P_2RuS$: C 53.41%, H 7.73%, N 1.56%; found, C 53.42%, H 7.88%, N 1.78%.

Synthesis of [RuC(Cl)(CN)(PCy$_3$)$_2$] (RuC-CN). KCN (17.8 mg, 273 μmol) and **RuC-MeCN** (15.0 mg, 16.7 μmol) were placed in 1 mL of acetonitrile and stirred for 24 h whereupon **RuC-CN** precipitated. The suspension was passed through a plug of silica (diameter 0.5 cm, length 2 cm), and the residue was washed with acetonitrile (5 × 1 mL) and extracted with dichloromethane (5 × 1 mL). The dichloromethane was evaporated to afford **RuC-CN** as a white powder. Yield: 9.9 mg, 13.5 μmol, 80.7% based on **RuC-MeCN**. Crystals suitable for X-ray crystallography were grown by concentrating an acetonitrile solution of **RuC-CN**. ^{1}H NMR, 500 MHz, $CDCl_3$, δ: 2.70−2.60 (m, 6H), 2.28−2.20 (m, 6H), 2.14−2.06 (m, 6H), 1.91−1.81 (m, 12H), 1.78−1.70 (m, 6H), 1.64−1.46 (m, 12H), 1.38−1.20 (m, 18H). ^{13}C NMR, 126 MHz, $CDCl_3$, δ: 474.91, 132.69 (t, $^{2}J_{C-P}$ = 13.7 Hz), 33.16 (virtual t, $^{1}J_{C-P}$ = 10.5 Hz), 30.56, 29.83, 27.99 (virtual t, $^{1}J_{C-P}$ = 5.4 Hz), 26.70. ^{31}P NMR, 202 MHz, $CDCl_3$, δ: 44.78 (d, *J* = 13.8 Hz). ESI^{+} MS, CH_3CN, *m*/*z*, f/c: [RuC(MeCN)(CN)(PCy$_3$)$_2$]$^{+}$: 741.41/741.40, [RuC(CN)(PCy$_3$)$_2$]$^{+}$: 700.38/700.37. Anal. Calcd for $C_{38}H_{66}ClNP_2Ru$: C 62.06%, H 9.05%, N 1.90%; found, C 61.98%, H 9.38%, N 1.83%.

Synthesis of [RuC(Cl)(F)(PCy$_3$)$_2$] (RuC-F). In a plastic test tube, an acetonitrile solution (0.5 mL) of (Et$_4$N)F·H$_2$O (7.2 mg, 43 μmol, 2.8 equiv) was added to an acetonitrile solution (1 mL) of **RuC-MeCN** (13.7 mg, 15.2 μmol). Within 10 min, yellow crystals of **RuC-F** were deposited on the walls of the test tube. The mother liquor was decanted off, and the crystals were washed with acetonitrile (3 × 1 mL) and dried in vacuo. Yield: 3.9 mg, 5.4 μmol, 35.2% based on **RuC**. ^{1}H NMR, 500 MHz, C_6D_6, δ: 2.54−2.45 (m, 6H), 2.42−2.35 (m, 6H), 2.35−2.27 (m, 6H), 1.92−1.78 (m, 12H), 1.78−1.70 (m, 12H), 1.62−1.56 (m, 6H), 1.26−1.15 (m, 18H). ^{13}C NMR, 126 MHz, C_6D_6, δ: 474.58 (d, $^{2}J_{C-F}$ = 24.4 Hz), 32.21 (virtual t, $^{1}J_{C-P}$ = 9.6 Hz), 30.08, 29.84, 28.16 (virtual t, $^{1}J_{C-P}$ = 5.5 Hz), 28.09 (virtual t, $^{1}J_{C-P}$ = 5.0 Hz), 26.92. ^{31}P NMR, 202 MHz, C_6D_6, δ: 37.76 (d, $^{2}J_{P-F}$ = 12.5 Hz). ^{19}F-NMR, 282 MHz, C_6D_6, δ: − 423.39 (t, $^{2}J_{F-P}$ = 18.7 Hz). Anal. Calcd for $C_{37}H_{66}ClFP_2Ru$·0.10 CH_3CN: C 61.00%, H 9.12%, N 0.19; found, C 60.81%, H 8.94%, N 0.14%.

Synthesis of [RuC(Cl)(X)(PCy$_3$)$_2$] (RuC-X). The syntheses of the remaining **RuC-X** systems were carried out essentially as described for **RuC-CN**. KI and KNCS are slightly soluble in acetonitrile, and in the dichloromethane extracts, these salts consequently appeared as cloudy precipitates that were removed by filtration. Alternatively, the approach used to obtain **RuC-F** was generally applicable to the other **RuC-X** systems (salts of PPh_4^{+} were used in place of (Et$_4$N)F·H$_2$O; (PPh$_4$)(CN), however, is not suitable for this procedure).

RuC-Br: ^{1}H NMR, 500 MHz, $CDCl_3$, δ 2.74−2.63 (m, 6H), 2.23−2.12 (m, 12H), 1.90−1.78 (m, 12H), 1.76−1.70 (m, 6H), 1.70−1.56 (m, 12H), 1.33−1.22 (m, 18H). ^{13}C NMR, 126 MHz, $CDCl_3$, δ: 471.38 (t, $^{2}J_{C-P}$ = 3.7 Hz), 32.39 (virtual t, $^{1}J_{C-P}$ = 10.1 Hz), 30.32, 30.26, 28.17 (virtual t, $^{1}J_{C-P}$ = 4.9 Hz), 28.15 (virtual t, $^{1}J_{C-P}$ = 5.1 Hz), 26.85. ^{31}P NMR, 202 MHz, $CDCl_3$, δ: 37.89. Anal. Calcd for $C_{37}H_{66}BrClP_2Ru$: C 56.30%, H 8.43%; found, C 56.65%, H 8.60%.

RuC-I: ^{1}H NMR, 500 MHz, $CDCl_3$, δ 2.89−2.74 (m, 6H), 2.27−2.10 (m, 12H), 1.93−1.77 (m, 12H), 1.77−1.60 (m, 12H), 1.58−1.47 (m, 6H), 1.34−1.20 (m, 18H). ^{13}C NMR, 126 MHz, $CDCl_3$, δ: 469.74 (t, $^{2}J_{C-P}$ = 3.6 Hz), 33.44 (virtual t, $^{1}J_{C-P}$ = 10.0 Hz), 30.92, 30.50, 28.18 (virtual t, $^{1}J_{C-P}$ = 5.2 Hz), 28.14 (virtual t, $^{1}J_{C-P}$ = 4.7 Hz), 26.85. ^{31}P NMR, 202 MHz, $CDCl_3$, δ: 38.47. Anal. Calcd for

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$C_{37}H_{66}ClIP_2Ru \cdot 3/4\ CH_3CN$: C 53.33%, H 7.93%, N 1.21%; found, C 53.76%, H 8.00%, N 1.09%.

RuC-NCO: ^{1}H NMR, 500 MHz, $CDCl_3$, δ 2.49−2.37 (m, 6H), 2.23−2.08 (m, 12H), 1.93−1.81 (m, 12H), 1.79−1.69 (m, 6H), 1.68−1.49 (m, 12H), 1.37−1.21 (m, 18H). ^{13}C NMR, 126 MHz, $CDCl_3$, δ: 473.51 (t, $^2J_{C-P}$ = 3.8 Hz), 134.41, 32.24 (virtual t, $^1J_{C-P}$ = 9.8 Hz), 29.93, 28.08 (virtual t, $^1J_{C-P}$ = 5.1 Hz), 28.04 (virtual t, $^1J_{C-P}$ = 4.9 Hz), 26.74. ^{31}P NMR, 202 MHz, $CDCl_3$, δ: 41.23. Anal. Calcd for $C_{38}H_{66}ClNOP_2Ru$: C 60.74%, H 8.85%, N 1.86%; found, C 60.78%, H 9.06, N 2.00%.

RuC-NCS: ^{1}H NMR, 500 MHz, $CDCl_3$, δ: 2.51−2.39 (m, 6H), 2.23−2.15 (m, 6H), 2.15−2.06 (m, 6H), 1.92−1.83 (m, 12H), 1.80−1.71 (m, 6H), 1.69−1.58 (m, 6H), 1.58−1.47 (m, 6H), 1.41−1.22 (m, 18H). ^{13}C NMR, 126 MHz, $CDCl_3$, δ: 477.50, 149.43, 32.44 (virtual t, $^1J_{C-P}$ = 10.1 Hz), 30.09, 29.81, 28.15 (virtual t, $^1J_{C-P}$ 5.4 Hz), 28.01 (virtual t, $^1J_{C-P}$ = 5.2 Hz), 26.71. ^{31}P NMR, 202 MHz, $CDCl_3$, δ: 42.73. Anal. Calcd for $C_{38}H_{66}ClNP_2RuS$: C 59.47%, H 8.67%, N 1.83%; found, C 58.93%, H 8.87%, N 1.76%.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00803.

Description of physical methods; molecular structure plots and crystallographic information for **RuC-Br**, **RuC-CN**, **RuC-NCO**, and $[Ru(PCy_3)_2(CN)_4]^{2-}$; details of computations; and additional kinetic data and selected NMR spectra (PDF)

Crystallographic data for **RuC-Br**, **RuC-CN**, **RuC-NCO**, and $[Ru(PCy_3)_2(CN)_4]^{2-}$ (ZIP)

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Notes

The authors declare no competing financial interest.

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