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Synthetic and mechanistic studies on ruthenium dicarbonyl complexes containing $PhP(CH_2CH_2CH_2PCy_2)_2$ (Cyttp) ligand

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Dedicated to Professor Fred Basolo, a pioneer of mechanistic inorganic chemistry, with our respect and best wishes on the occasion of his 85th birthday

Abstract

A synthetic and mechanistic study is reported on ligand substitution and other reactions of six-coordinate ruthenium(II) carbonyl complexes containing tridentate $PhP(CH_2CH_2CH_2PCy_2)_2$ (Cyttp). Carbonylation of *cis-mer*-$Ru(OSO_2CF_3)_2(CO)$(Cyttp) (**1**) affords [*cis-mer*-$Ru(OSO_2CF_3)(CO)_2$(Cyttp)]O_3SCF_3 (**2**(O_3SCF_3)) and, on longer reaction times, [*cis-mer*-Ru(solvent)$(CO)_2$(Cyttp)]$(O_3SCF_3)_2$ (solvent = acetone, THF, methanol). **2**(O_3SCF_3) reacts with each of NaF, LiCl, LiBr, NaI, and $LiHBEt_3$ to yield [*cis-mer*-$RuX(CO)_2$(Cyttp)]$^+$ (X = F (**3**), Cl (**4**), Br (**5**), I (**6**), H (**7**)), isolated as **3**–**7**(BPh_4). These conversions proceed with high stereospecificity to afford only a single isomer of the product that is assigned a structure in which the Ph group of Cyttp points toward the CO *trans* to X (*anti* when X = F, Cl, Br, or I; *syn* when X = H). Treatment of **2**(O_3SCF_3) with NaOMe and CO generates the methoxycarbonyl complex [*cis-mer*-$Ru(CO_2Me)(CO)_2$(Cyttp)]$^+$ (**8**), whereas addition of excess *n*-BuLi to **2**(O_3SCF_3) in THF under CO affords *mer*-$Ru(CO)_2$(Cyttp) (**9**). The two ^{13}C isotopomers [*cis-mer*-$Ru(OSO_2CF_3)(CO)(^{13}CO)$(Cyttp)]$O_3SCF_3$ (**2′**(O_3SCF_3): ^{13}CO *trans* to P_C; **2″**(O_3SCF_3): ^{13}CO *cis* to all P donors) were synthesized by appropriate adaptations of known transformations and used in mechanistic studies of reactions with each of $LiHBEt_3$, NaOMe/CO, and *n*-BuLi. Whereas $LiHBEt_3$ reacts with **2′**(O_3SCF_3) and **2″**(O_3SCF_3) to replace triflate by hydride without any scrambling of the carbonyl ligands, the corresponding reactions of NaOMe–CO are more complex. The methoxide combines with the CO *cis* to triflate in **2**, and the resultant methoxycarbonyl ligand ends up positioned *trans* to the incoming CO in **8**. A mechanism is proposed for this transformation. Finally, treatment of either **2′**(O_3SCF_3) or **2″**(O_3SCF_3) with an excess of *n*-BuLi leads to the formation of the same two ruthenium(0) isomers of *mer*-$Ru(CO)(^{13}CO)$(Cyttp). These products represent, to our knowledge, the first example of a *syn–anti* pair of isomers of a five-coordinate metal complex.

Keywords: Ruthenium complexes; Carbonyl complexes; Triphosphine complexes; *syn–anti* Isomerism; Ligand substitution; Isotope effects; Mechanism

1. Introduction

We have previously reported synthesis and ligand substitution reactions of six-coordinate ruthenium(II) carbonyl complexes containing the tridentate phosphine $PhP(CH_2CH_2CH_2PCy_2)_2$ (Cyttp) and weakly coordinated anions, BF_4^- or $CF_3SO_3^-$ [1,2]. A number of these complexes display high configurational stability, which allows stereochemical studies to be conducted on ligand substitution and coupling processes. For example, in this context we recently investigated *syn–anti* isomeric behavior of *cis-mer*-$RuX_2(CO)$(Cyttp) (X = various monodentate, X_2 = various bidentate anionic ligands); this type of geometric isomerism arises as a

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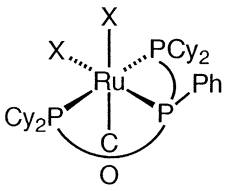
result of the Ph group on the central phosphorus atom being directed toward either X or CO [2] (cf. **I** and **II**). [1] Here, we describe the preparation of [*cis-mer*-$Ru(OSO_2CF_3)(CO)_2(Cyttp)]O_3SCF_3$ (**2**(O_3SCF_3)) and its ligand substitution, coupling (migratory insertion) and reduction reactions.



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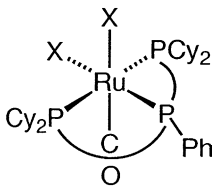


II

2. Experimental

2.1. General procedures and measurements

Reactions and manipulations of air-sensitive compounds were conducted at room temperature under an atmosphere of dry argon by use of standard procedures [4]. Solvents were dried [5], distilled under argon, and degassed before use. Elemental analyses were carried out by M–H-W Laboratories, Phoenix, AZ. IR, NMR (^1H, ^{13}C, ^{19}F, and ^{31}P), and mass spectra (FAB-MS) were obtained as previously described [6,7]. All listed mass peaks are those of ions containing ^{102}Ru. Relative peak intensities are given with the assignments.

2.2. Materials

Reagents were procured from various commercial sources and used as received. ^{13}CO was obtained from Aldrich Chemical Co. The complexes *cis-mer*-$Ru(OSO_2CF_3)_2(CO)(Cyttp)$ (**1**) [1] and *cis-mer*-$RuH_2(\eta^2\text{-}H_2)(Cyttp)$ [8] were synthesized according to the literature methods.

2.3. Synthesis of various complexes [*cis-mer-RuX(CO)$_2$(Cyttp)*]$^+$

2.3.1. Preparation of [*cis-mer-Ru(OSO$_2$CF$_3$)(CO)$_2$(Cyttp)*]*O$_3$SCF$_3$* (**2**(*O$_3$SCF$_3$*))

Carbon monoxide was passed through a stirred solution of *cis-mer*-$Ru(OSO_2CF_3)_2(CO)(Cyttp)$ (**1**) (0.213 g, 0.210 mmol) in 15 ml of acetone for 15 min. A $^{31}P\{^1H\}$ NMR spectrum indicated that all of **1** had been converted to product. Solvent was then removed, and the residue was washed with 25 ml of hexane and dried overnight under vacuum. Yield of **2**(O_3SCF_3), 0.208 g (95%). Selected spectroscopic properties. IR (Nujol): ν(C≡O) 2060 (s), 1993 (s) cm^{-1}. $^{13}C\{^1H\}$ NMR (acetone-d_6): δ (ppm) 198.6 (q, $^2J_{PC}$ = 12 Hz, CO *cis* to 3 P donors), 192.2 (dt, $^2J_{PC}$ = 83, 10 Hz, CO *trans* to P_C). $^{19}F\{^1H\}$ NMR (acetone-d_6): δ (ppm, referenced to internal $CFCl_3$) −77.3 (s, $RuOSO_2CF_3$), −79.0 (s, $CF_3SO_3^-$). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ (ppm) 11.4 (d, $^2J_{PP}$ = 33.8 Hz, P_W (wing P)), −2.7 (t, $^2J_{PP}$ = 33.8 Hz, P_C (central P)).

When this reaction was allowed to proceed for ca. 2 weeks, the $^{19}F\{^1H\}$ resonance at δ −77.3 ppm almost completely disappeared, and that at δ −79.0 ppm increased in intensity. Also, the $^{31}P\{^1H\}$ NMR signals of **2**(O_3SCF_3) at δ 11.4 and −2.7 ppm were barely discernible, and new intense signals occurred at δ 12.0 ppm (d, $^2J_{PP}$ = 33.5 Hz, P_W) and −6.7 ppm (t, $^2J_{PP}$ = 33.5 Hz, P_C). The new resonances most likely indicate formation of [*cis-mer*-Ru(acetone)$(CO)_2$(Cyttp)]$(O_3SCF_3)_2$. A similar behavior of **1** upon carbonylation was observed in THF or MeOH as indicated by $^{31}P\{^1H\}$ NMR spectroscopy.

2.3.2. Preparation of [*cis-mer-anti-RuF(CO)$_2$(Cyttp)*]*BPh$_4$* (**3**(*BPh$_4$*))

After carbon monoxide had been passed through a stirred solution of **1** (0.194 g, 0.191 mmol) in 40 ml of acetone for 1 h, NaF (0.110 g, 2.62 mmol) in 10 ml of H_2O was added, and the mixture was stirred for an additional hour. All volatiles were removed under vacuum, MeOH (20 ml) was added to dissolve the residue, and a solution of $NaBPh_4$ (0.200 g, 0.584 mmol) in 3 ml of MeOH was introduced with stirring to effect the precipitation of a fluffy white solid. The addition of 20 ml of H_2O induced further precipitation. After 5 min of stirring, the white solid was filtered off, washed consecutively with 20 ml of H_2O and 2 × 20 ml of hexane, and dried under vacuum overnight. Yield of **3**(BPh_4), 0.155 g (85%). The IR and $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopic properties of the product compare well with those of **3**(BF_4), prepared by a different reaction [1]. IR (CH_2Cl_2): ν(C≡O) 2048 (s), 1980 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ (ppm) 14.8 (dd, $^2J_{PP}$ = 36 Hz, $^2J_{PF}$ = 25 Hz, P_W), −0.8 (dt, $^2J_{PF}$ = 43 Hz, $^2J_{PP}$ = 36 Hz, P_C). FAB-MS: *m/z* 763 (M^+, 4), 735 (M^+ − CO, 100), 716 (M^+ − CO − F, 5).

2.3.3. Preparation of [*cis-mer-anti-RuCl(CO)$_2$(Cyttp)*]*BPh$_4$* (**4**(*BPh$_4$*))

A procedure analogous to that for **3**(BPh_4) in Section 2.3.2 was followed, using **1** (0.195 g, 0.192 mmol), CO, and LiCl (0.040 g, 0.94 mmol) in place of NaF, and employing a shorter reaction time (2 × 30 min instead

[1] The designation *syn* and *anti* is made in accordance with the Cahn–Ingold–Prelog priority rules [3] as applied to the two different ligands that are *trans* (X and CO in *cis-mer*-$RuX_2(CO)(Cyttp)$).

of 2 × 1 h). Yield of **4**(BPh_4), a white solid, 0.202 g (96%). Selected spectroscopic properties. IR (CH_2Cl_2): ν(C≡O) 2052 (s), 1991 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ (ppm) 10.5 (d, $^2J_{PP}$ = 35 Hz, P_W), −7.5 (t, $^2J_{PP}$ = 35 Hz, P_C). FAB-MS: *m/z* 779 (M^+, 5), 751 ($M^+ - CO$, 100), 716 ($M^+ - CO - {}^{35}Cl$, 5).

2.3.4. Preparation of [cis-mer-anti-RuBr(CO)$_2$(Cyttp)]-BPh_4 (**5**(BPh_4))

The title complex was prepared from **1** (0.163 g, 0.161 mmol), CO, and excess LiBr by a procedure analogous to that for **4**(BPh_4) in Section 2.3.3. Yield of **5**(BPh_4), 0.168 g (91%). The IR and $^{31}P\{^1H\}$ NMR spectroscopic properties of the cation match those previously reported for **5**(AsF_6) [9]. IR (CH_2Cl_2): ν(C≡O) 2052 (s), 1993 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ (ppm) 7.4 (d, $^2J_{PP}$ = 35 Hz, P_W), −11.8 (t, $^2J_{PP}$ = 35 Hz, P_C). FAB-MS: *m/z* 823 (M^+, 8), 795 ($M^+ - CO$, 100), 716 ($M^+ - CO - Br$, 6).

2.3.5. Preparation of [cis-mer-anti-RuI(CO)$_2$(Cyttp)]-BPh_4 (**6**(BPh_4))

A procedure analogous to that for **4**(BPh_4) in Section 2.3.3 was employed, with NaI replacing NaF. Yield of **6**(BPh_4), 93%. The IR and $^{31}P\{^1H\}$ NMR spectroscopic properties of the cation match those previously reported for **6**(I) [9]. IR (CH_2Cl_2): ν(C≡O) 2051 (s), 1995 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ (ppm) 2.7 (d, $^2J_{PP}$ = 35 Hz, P_W), −18.1 (t, $^2J_{PP}$ = 35 Hz, P_C.) FAB-MS: *m/z* 871 (M^+, 16), 843 ($M^+ - CO$, 100), 716 ($M^+ - CO - I$, 9).

2.3.6. Preparation of [cis-mer-syn-RuH(CO)$_2$(Cyttp)]-BPh_4 (**7**(BPh_4))

The title hydrido complex was prepared from **1** (0.088 g, 0.087 mmol), CO, and $LiHBEt_3$ (0.17 ml of 1 M solution in THF) in 30 ml of THF by a procedure analogous to that for **4**(BPh_4) in Section 2.3.3. Yield of **7**(BPh_4), a white solid, 0.075 g (81%). The IR and ^1H and $^{31}P\{^1H\}$ NMR spectroscopic properties of the cation match those previously reported for **7**(BF_4) and **7**(AsF_6) [9].

2.3.7. Preparation of [cis-mer-Ru(CO$_2$Me)(CO)$_2$(Cyttp)]-BPh_4 (**8**(BPh_4))

A solution of **1** (0.200 g, 0.197 mmol) in 10 ml of MeOH was treated with gaseous CO for 30 min, and NaOMe (0.20 mmol) in MeOH was added dropwise. The contents were stirred for 1 h under CO, and a solution of $NaBPh_4$ (0.10 g, 0.30 mmol) in ca. 2 ml of MeOH was added to induce the precipitation of a fluffy white solid. The volume of the reaction mixture was reduced to ca. 5 ml, and H_2O (10 ml) was introduced with stirring. The white product was filtered off, washed with two 20-ml portions of hexane, and dried under vacuum overnight. Yield of **8**(BPh_4), 0.198 g (90%). Selected spectroscopic properties. IR (Nujol): ν(C≡O) 2030 (s), 1992 (s), ν(C=O) 1628 (s), ν(C–O) 1027 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ (ppm) 3.54 (s, OMe). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 198.9 (dt, $^2J_{PC}$ = 13.8, 11.4 Hz, *C*OMe), 198.4 (q, $^2J_{PC}$ = 9.3 Hz, CO *cis* to 3 P donors), 195.4 (dt, $^2J_{PC}$ = 76.5, 11.1, Hz, CO *trans* to P_C), 50.6 (s, CO*Me*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 12.2 (d, $^2J_{PP}$ = 37.3 Hz, P_W), −10.1 (t, $^2J_{PP}$ = 37.3 Hz, P_C). *Anal.* Calc. for $C_{64}H_{84}BO_4P_3Ru$: C, 68.50; H, 7.55. Found: C, 68.33; H, 7.68%.

2.4. Reaction of [cis-mer-Ru(OSO$_2$CF$_3$)(CO)$_2$(Cyttp)]-O_3SCF_3 (**2**(O_3SCF_3)) with n-BuLi

Carbon monoxide was passed through a stirred solution of **1** (0.053 g, 0.052 mmol) in 10 ml of THF for 30 min, and the contents were treated with *n*-BuLi in hexane (0.10 ml, 1.6 M, 0.16 mmol). The colorless reaction mixture turned bright yellow, and a $^{31}P\{^1H\}$ NMR spectrum indicated complete conversion of **2**(O_3SCF_3) to known [9] *mer*-Ru(CO)$_2$(Cyttp) (**9**). Solvent was evaporated, and the residue was extracted with 5 ml of hexane to remove excess *n*-BuLi. The remaining solid was dissolved in 5 ml of benzene, the solution was filtered through a 2-cm pad of Celite, and the yellow filtrate was evaporated to dryness. Yield of **9**, 0.031 g (80%).

2.5. Synthesis of isomers of [cis-mer-Ru(OSO$_2$CF$_3$)(CO)(^{13}CO)(Cyttp)]O_3SCF_3 (**2′**(O_3SCF_3)) and (**2″**(O_3SCF_3))

2.5.1. Preparation of [cis-mer-Ru(OSO$_2$CF$_3$)(CO)(^{13}CO-trans to P_C)(Cyttp)] O_3SCF_3 (**2′**(O_3SCF_3))

To a partially evacuated Schlenk flask containing a solution of **1** in the appropriate solvent (acetone, THF, or MeOH) under argon was introduced gaseous CO enriched ca. 70% in carbon-13. The flask was closed, and the contents were stirred for ca. 15 min. The pressure was then returned to 1 atm by introduction of additional ^{13}CO. This procedure was repeated until $^{31}P\{^1H\}$ NMR spectroscopy indicated a complete conversion of **1** to **2′**(O_3SCF_3).

2.5.2. Preparation of [cis-mer-Ru(OSO$_2$CF$_3$)(CO)(^{13}CO-cis to all P donors)(Cyttp)] O_3SCF_3 (**2″**(O_3SCF_3))

A solution of *cis-mer*-$RuH_2(\eta^2\text{-}H_2)$(Cyttp) [8] in hexane was maintained under an atmosphere of ^{13}CO in a Schlenk flask. Large colorless crystals began to form on the sides of the flask in ca. 24 h. After 48 h, the crystals were collected on a filter frit, dried, and identified spectroscopically as *cis-mer-syn*-$RuH_2(^{13}CO)$(Cyttp) [8]. Reaction of the isolated carbonyl dihydride with CF_3SO_3H according to the literature [1] afforded *cis-mer*-Ru(OSO$_2$CF$_3$)$_2$(^{13}CO)(Cyttp) (**1′**) in high yield (⩾90%). Complex **1′** was converted to **2″**(O_3SCF_3) by

carbonylation with CO of natural isotopic abundance as described in Section 2.3.1.

3. Results and discussion

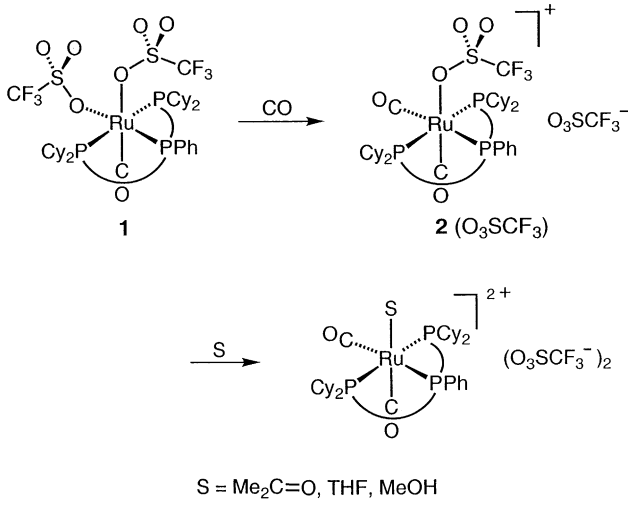
3.1. Carbonylation of cis-mer-Ru(OSO_2CF_3)$_2$(CO)(Cyttp) (1)

Bubbling carbon monoxide through a solution of **1** in acetone at room temperature leads to rapid replacement of the triflate ligand *trans* to the central phosphorus atom (P_C) of the Cyttp (Scheme 1). This is indicated by the appearance of a new A_2X set of $^{31}P\{^1H\}$ NMR signals in which the resonance of P_C occurs upfield relative to that of P_W (wing phosphorus), a characteristic of strong *trans*-influence ligands opposite P_C [10]. After ca. 15 min, the solvent was removed, and the product [*cis-mer*-Ru(OSO_2CF_3)(CO)$_2$(Cyttp)]O_3SCF_3 (**2**(O_3SCF_3)) was isolated in 95% yield. Its assigned structure is supported by spectroscopic data (cf. Section 2.3.1). The IR spectrum shows two equal-intensity ν(C≡O) bands at 2060 and 1993 cm^{-1}, and the $^{13}C\{^1H\}$ NMR spectrum displays two low-field resonances at δ 198.6 ppm as a quartet (CO *cis* to three P donors) and δ 192.2 ppm as a doublet of triplets (CO *trans* to P_C). The $^{19}F\{^1H\}$ NMR spectrum consists of two singlets of approximately equal intensity at δ −77.3 and −79.0 ppm, in agreement with the presence of one covalent and one ionic triflate [11].

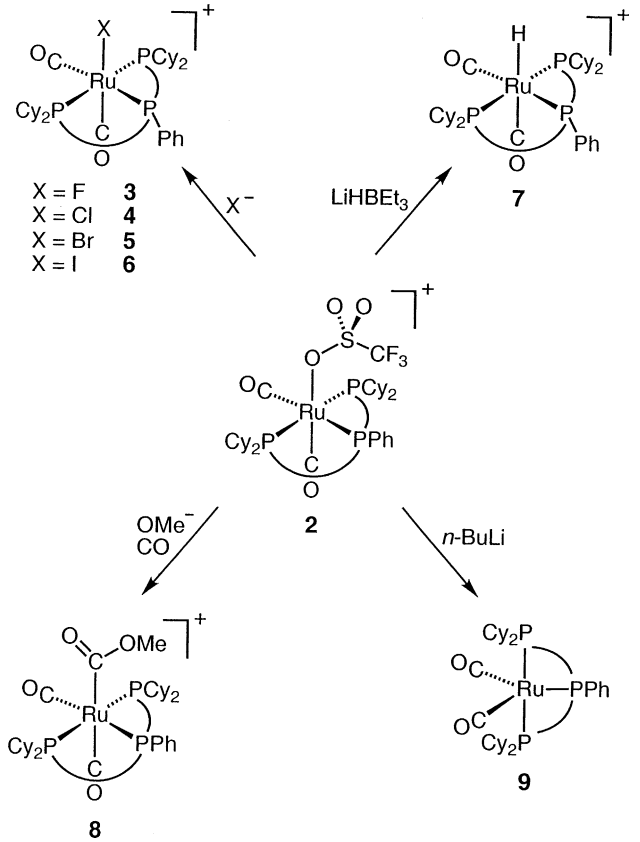
When the reaction is allowed to proceed for a longer time, the $^{19}F\{^1H\}$ NMR signal at δ −77.3 ppm decreases in intensity while that at δ −79.0 ppm becomes stronger. Accompanying this change is the appearance and growth of a new AX_2 set of $^{31}P\{^1H\}$ resonances at δ 12.0 and −6.7 ppm with a $^2J_{PP}$ similar to that of **2**(O_3SCF_3), and the simultaneous decrease in intensity of the resonances at δ 11.4 and −2.7 ppm of **2**(O_3SCF_3). After 2 weeks, the $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra indicate essentially complete conversion of **2**(O_3SCF_3) to a new, structurally similar product, formulated as the solvento complex [*cis-mer*-Ru(acetone)(CO)$_2$(Cyttp)](O_3SCF_3)$_2$ (Scheme 1). Carbonylation of **1** in THF or methanol solution proceeds similarly.

3.2. Reactions of [cis-mer-Ru(OSO_2CF_3)(CO)$_2$(Cyttp)](O_3SCF_3) (**2**(O_3SCF_3)) with nucleophiles

The presence of weakly coordinating triflate in **2** suggests that this complex should undergo facile substitution reactions. Indeed, **2**(O_3SCF_3) generated in situ from **1** and CO reacts readily with each of NaF, LiCl, LiBr, and NaI to afford the respective [*cis-mer-anti*-RuX(CO)$_2$(Cyttp)]$^+$ (**3**–**6**) (Scheme 2). Similarly, the hydride [*cis-mer-syn*-RuH(CO)$_2$(Cyttp)]$^+$ (**7**) was obtained from **2**(O_3SCF_3) and $LiHBEt_3$. All of the complexes **3**–**7** were isolated in 81–96% yield as the BPh_4^- salts by anion metathesis in MeOH. Complexes **3** [1] and **5**–**7** [9] were reported previously, but their synthesis involved different reactions, mostly oxidation of *mer*-Ru(CO)$_2$(Cyttp) (**9**). For example, **7** was obtained by



Scheme 1.



Scheme 2.

treatment of **9** with $HBF_4 \cdot Et_2O$ or HX (X = Cl or Br). ^1H NMR nOe experiments on **7**(BPh_4) in which each of the phenyl resonances (*o*, *m*, and *p*) of the Cyttp ligand was irradiated show no enhancement of intensity of the RuH hydride signal. These experiments suggest that the complex exists as the *syn* isomer, with the phenyl ring directed away from the hydride ligand and toward the *trans* CO. Similar ^1H NMR nOe experiments were used previously to assign structures to *syn* and *anti* isomers of related hydrido metal complexes [9,12]. Since the halide complexes **3**–**6** were prepared by analogous ligand substitution reactions of **2**(O_3SCF_3), and their spectroscopic properties indicate the presence of only one isomer, they likewise are assigned structures in which the Cyttp phenyl group is oriented away from the halide and toward the *trans* CO (i.e., *anti*).

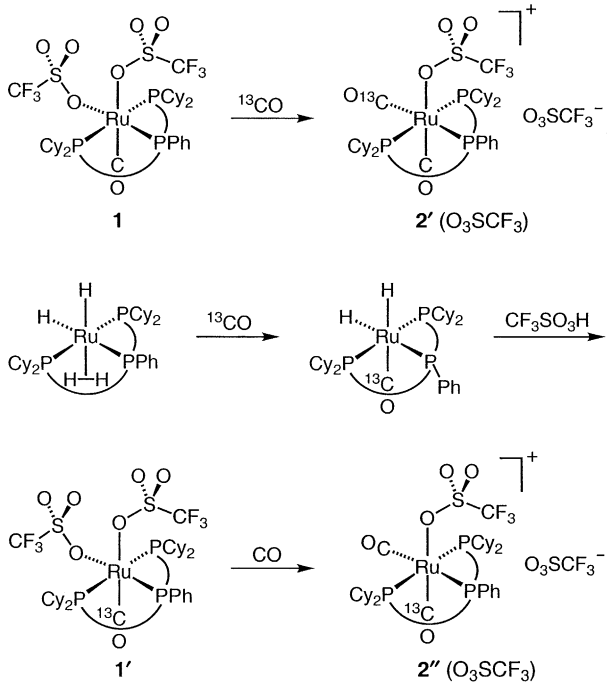
The IR ν(C≡O) values of the complexes **3**–**6**(BPh_4) show little sensitivity to the halide ligand; a similar behavior has been noted for the series PPN[WX(CO)$_5$] (PPN = Ph_2N; X = F, Cl, Br, I) [13]. In the $^{31}P\{^1H\}$ NMR spectra of the BPh_4^- salts of **3**–**6**, the chemical shifts of the ^{31}P nuclei move upfield as X varies from F to I to indicate increased shielding owing to polarizability of the halide [14]. A parallel trend has been reported for the complexes [*mer*-Re(X)(F)(O)(Cyttp)]BPh_4 (X = F, Cl, Br) where X and F are *cis* [15]. FAB-MS data for the BPh^- salts of **3**–**6** show similar fragmentation patterns for the metal complex cation, with $[M^+ - CO]$ being the most predominant ion detected in each case.

Complex **2**(O_3SCF_3) reacts with NaOMe in methanol under an atmosphere of CO to form a new methoxycarbonyl product, [*cis*-*mer*-Ru(CO_2Me)(CO)$_2$(Cyttp)]$^+$ (**8**) (Scheme 2), which was isolated analytically pure in excellent yield as **8**(BPh_4), after anion metathesis using $NaBPh_4$. The $^{31}P\{^1H\}$ NMR spectrum of **8**(BPh_4) (Section 2.3.7), an AX_2 pattern, is similar to the spectra of the halide complexes **3**–**6**(BPh_4), and the IR spectrum shows two strong ν(C≡O) bands at 2030 and 1992 cm^{-1} to demonstrate a *cis* structure. The presence of two inequivalent carbonyl ligands is reflected by the appearance of $^{13}C\{^1H\}$ NMR signals at δ 198.4 (q, $^2J_{PC}$ = 9.3 Hz) and 195.4 (dt, $^2J_{PC}$ = 76.5, 11.1 Hz). There is also a O=C resonance of the methoxycarbonyl group at δ 198.9 ppm (dt, $^2J_{PC}$ = 13.8, 11.4 Hz), assigned from the spectrum of the ^{13}CO-enriched product (cf. Section 3.3). The angle 2θ between the carbonyl ligands was calculated to be 85° by use of the equation I(sym)/I(asym) = $\cot^2\theta$ where I(sym)/I(asym) stands for the ratio of the appropriate band intensities [16].

Reaction between **2**(O_3SCF_3) and *n*-BuLi in excess in THF solution under CO leads to reduction of the metal to yield *mer*-Ru(CO)$_2$(Cyttp) (**9**) as the only Cyttp-containing product (Scheme 2). Reduction of related ruthenium(II) complexes with RLi, e.g., of $[Ru(CO)_2(ttp)]^{2+}$ (ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$) with MeLi, has been reported [9].

3.3. Mechanistic studies on reactions of ^{13}CO-labeled [*cis*-*mer*-Ru(OSO_2CF_3)(CO)$_2$(Cyttp)]O_3SCF_3 (**2′**(O_3SCF_3) and **2″**(O_3SCF_3))

To gain insight into mechanistic aspects of some reactions of **2**(O_3SCF_3) presented in Section 3.2, we investigated stereochemical behavior of the ^{13}CO-labeled **2′**(O_3SCF_3) and **2″**(O_3SCF_3). These two isotopomers were prepared by stereospecific incorporation of ^{13}CO into the coordination sphere of ruthenium through use of known reactions (Scheme 3). Thus, **2′**(O_3SCF_3), containing ^{13}CO *trans* to the P_C of Cyttp, was obtained by carrying out the conversion of **1** to **2**(O_3SCF_3) (cf. Section 2.3.1), but with ^{13}CO instead of ^{12}CO. The incoming ^{13}CO ligand ends up exclusively in the coordination site formerly occupied by the replaced triflate, while the positions of the remaining ligands are not affected. This is indicated by the splitting patterns and relative values of various $^2J_{PC}$ in the $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra. The former spectrum shows a doublet of doublets ($^2J_{PwC}$ = 9.9 Hz) at δ 11.4 ppm for P_W and a doublet ($^2J_{PcC}$ = 83 Hz) of triplets at δ −2.7 ppm for P_C ($^2J_{PP}$ = 33.8 Hz), whereas the latter displays a strong signal of the *trans*-to-P_C carbonyl carbon as a doublet of triplets at δ 192.2 ppm (cf. Section 3.1). The isotopomer **2″**(O_3SCF_3), containing ^{13}CO in a position *cis* to all three P donors, was synthesized in three steps starting with *cis*-*mer*-RuH_2(η^2-H_2)(Cyttp). Reaction of this polyhydride with ^{13}CO afforded *cis*-*mer*-*syn*-RuH_2(^{13}CO)(Cyttp), the ^{13}CO isotopomer of the known carbonyl dihydride [8]. The product was in turn



Scheme 3.

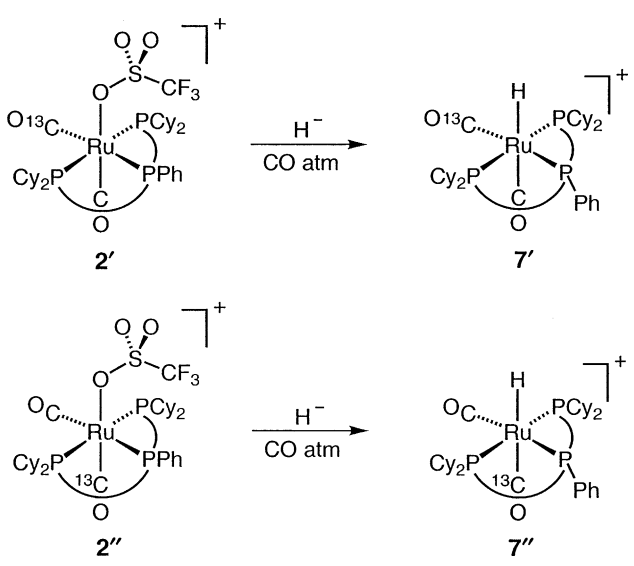
converted to *cis-mer*-$Ru(OSO_2CF_3)_2(^{13}CO)(Cyttp)$ (**1′**) by treatment with triflic acid [1]. Finally, carbonylation of **1′** with CO of natural isotopic abundance led to the substitution of the triflate *trans* to P_C to give **2″**(O_3SCF_3). The $^{31}P\{^1H\}$ NMR spectrum of **2″**(O_3SCF_3) shows some similarity to that of **2′**(O_3SCF_3) but displays nearly equal $^2J_{PC}$ values of $^2J_{PwC}$ = 11 Hz and $^2J_{PcC}$ = 12 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the strong signal of the ^{13}CO *trans* to triflate appears as an approximate quartet (doublet of triplets with $^2J_{PcC} \sim {}^2J_{PwC}$) at δ 198.6 ppm (cf. Section 3.1). All steps in the formation of **2″**(O_3SCF_3) proceed without any observable ligand scrambling. Also, when **2**(O_3SCF_3) doubly labeled with ^{13}CO was exposed to ^{12}CO for 2 weeks, no depletion of ^{13}CO was observed by $^{31}P\{^1H\}$ NMR spectroscopy to show that the carbonyl ligands are substitutionally inert at ambient temperature.

Complexes **2′**(O_3SCF_3) and **2″**(O_3SCF_3) lend themselves particularly well to mechanistic studies of reactions with nucleophiles owing to the spectroscopic handles provided by the ^{13}CO enrichment, the absence of scrambling between the CO's, and the apparent lack of lability of these two ligands. The fate of each CO can therefore be determined unambiguously by spectroscopy after reaction.

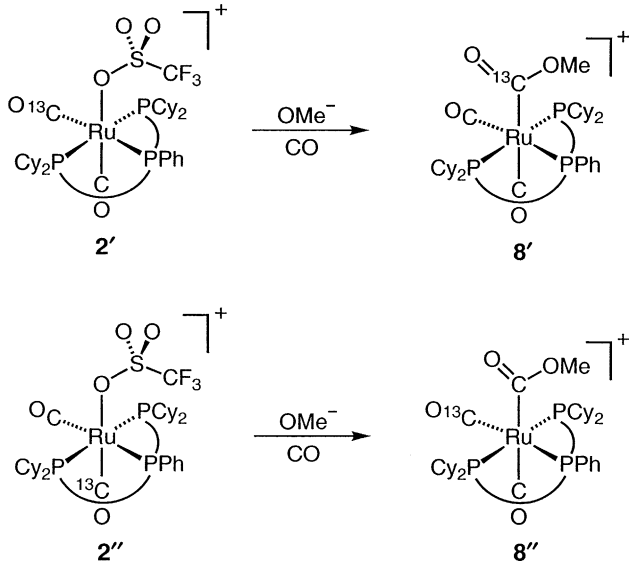
Reactions of **2′**(O_3SCF_3) and **2″**(O_3SCF_3) with $LiHBEt_3$ under CO are given in Scheme 4. Treatment of **2′**(O_3SCF_3) with an excess of $LiHBEt_3$ cleanly produces **7′**, isolated as **7′**(BPh_4). The ^1H, $^{13}C\{^1H\}$ (carbonyl region), and $^{31}P\{^1H\}$ NMR spectra of the product in $CDCl_3$ solution confirm that the ^{13}CO remains *trans* to P_C ($^2J_{PcC}$ = 72 Hz, $^2J_{PwC}$ = 13 Hz, $^2J_{CH}$ = 4 Hz). Similarly, reaction of **2″**(O_3SCF_3) with $LiHBEt_3$ yields exclusively **7″**, isolated as **7″**(BPh_4). The NMR spectra of this complex indicate that ^{13}CO is still positioned *cis* to the three P donors ($^2J_{PcC}$ = 9 Hz, $^2J_{PwC}$ = 6 Hz). The simplest mechanism that explains these results is direct substitution of ligated triflate by hydride; however, attack of hydride at the carbonyl *cis* to the triflate followed by replacement of the latter by the formyl hydrogen cannot be ruled out.

The reaction of **2′**(O_3SCF_3) with one equivalent of NaOMe in MeOH under an atmosphere of CO cleanly produces [*cis-mer*-$Ru(^{13}CO_2Me)(CO)_2(Cyttp)]^+$ (**8′**), isolated as **8′**(BPh_4) (Scheme 5). The presence of ^{13}C in the $^{13}CO_2Me$ ligand *cis* to the three P donor atoms is indicated by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR and IR spectroscopy. The ^1H NMR spectrum shows the OMe resonance at δ 3.53 ppm as a doublet ($^3J_{CH}$ = 3.7 Hz), and the $^{13}C\{^1H\}$ NMR spectrum reveals a strong (^{13}C enrichment) $^{13}CO_2Me$ resonance at δ 198.4 ppm as a doublet of triplets (cf. Section 2.3.7). The $^{31}P\{^1H\}$ NMR spectrum resembles that of **8**(BPh_4), except for an additional, similar doublet splitting of the P_C and P_W resonances owing to comparable values of $^2J_{PC}$. The IR ν(C≡O) bands are unaffected by ^{13}C labeling; however, the ν(C═O) band shifts from 1628 to 1591 cm^{-1}, and the ν(C–O) band from 1027 to 1017 cm^{-1}, as expected.

When **2″**(O_3SCF_3) was treated with a slight excess of NaOMe under the conditions that mirrored those for the corresponding reaction of **2′**(O_3SCF_3), [*cis-mer*-Ru(CO_2Me)(CO)(^{13}CO-*trans* to P_C)(Cyttp)]$^+$ (**8″**) and a small amount of **7′** were obtained. The $^{31}P\{^1H\}$ NMR spectrum of isolated **8″**(BPh_4) indicates that the ^{13}CO ligand has moved from a site *cis* to P_C in **2″** to the site *trans* to P_C ($^2J_{PcC}$ = 76 Hz, $^2J_{PwC}$ = 11 Hz). Complex **7′** most likely arises from reaction of **2″**(O_3SCF_3) with NaOH, present as an impurity in NaOMe. This side reaction may proceed similarly to that of **2″**(O_3SCF_3)



Scheme 4.

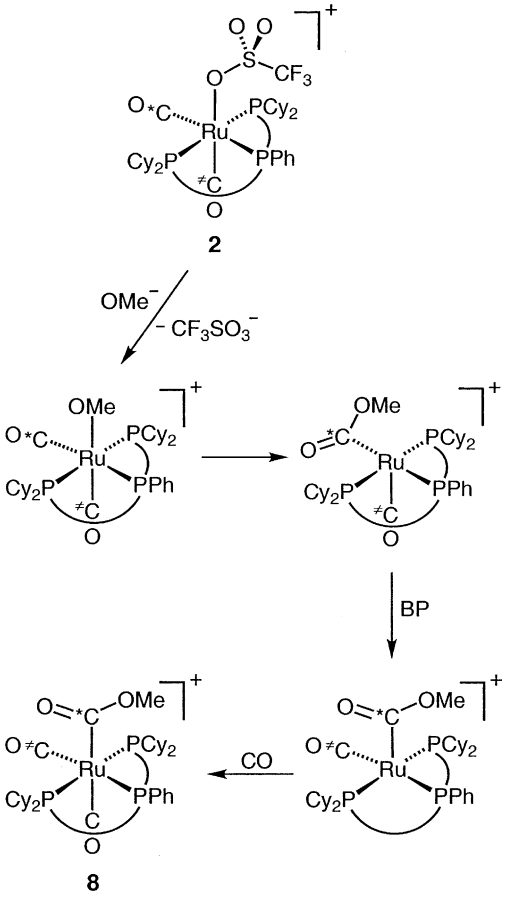


Scheme 5.

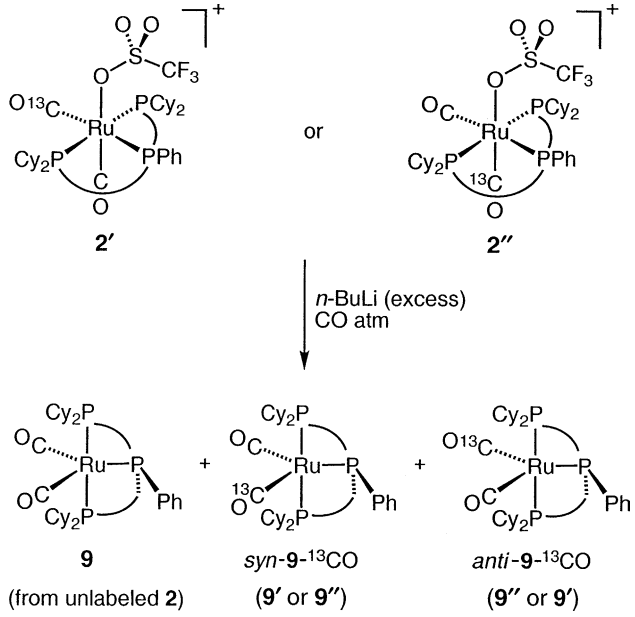
with NaOMe (vide infra), with the final step being decarboxylation of Ru-C(O)OH to Ru-H. Formation of M–H by reaction of M–CO with OH^- is a known transformation [17].

A possible mechanism of reaction of **2**(O_3SCF_3) (and its ^{13}C isotopomers) with NaOMe under CO atmosphere to yield **8**(O_3SCF_3) (and its ^{13}C isotopomers) is presented in Scheme 6 (the two inequivalent CO ligands in **2** are marked * and ≠). Based upon facile ligand substitution reactions of **2** with various nucleophiles X^- and of the related [*mer*-Ru(THF)(CO)($P(OMe)_3$)(Cyttp)]$^{2+}$ with OMe^- [1], we propose initial coordination of methoxide to the metal center. The next step would be migration of OMe^- onto the carbonyl *cis* to it (marked * in Scheme 6) to give a square-pyramidal intermediate, with the methoxycarbonyl in an equatorial position. This species then isomerizes by a Berry pseudorotation (BP) process [18], in which the C(O)OMe and CO ligands exchange positions. The driving force for the isomerization is to generate a more stable intermediate, with the stronger σ-bonding ligand C(O)OMe in an apical site and the stronger π-bonding ligand CO in an equatorial site [19]. The latter five-coordinate, 16-electron intermediate then combines with a CO present in the reaction system to yield **8** (or **8′** or **8″**). It is interesting that the ligand C(O)OMe and the incoming CO occupy *trans* positions in the product. Although migratory insertion reactions of CO and alkoxide have been little studied [20], in the related insertion involving CO and alkyl, the acyl ligand generated by coupling and the incoming ligand usually end up mutually *cis* [21]. There are, however, exceptions [22].

The reaction of either **2′**(O_3SCF_3) or **2″**(O_3SCF_3) with more than two equivalents of *n*-BuLi in THF under CO leads to reduction of the metal and formation of *mer*-Ru(CO)(^{13}CO)(Cyttp) (Scheme 7). The $^{31}P\{^1H\}$ NMR spectrum of the product complexes shows that three different species were generated: the unlabeled **9** (since **2**(O_3SCF_3) was not 100% enriched in ^{13}CO) and two isomers of *mer*-Ru(CO)(^{13}CO)(Cyttp), viz., *syn*-**9**-^{13}CO and *anti*-**9**-^{13}CO (**9′** and **9″**, with no specific stereochemical assignment). The carbonyl region $^{13}C\{^1H\}$ NMR spectrum confirms the presence of **9′** and **9″**. The appropriate NMR data are presented in Table 1. Three $^{31}P\{^1H\}$ NMR sets of signals (a doublet of triplets; two doublets of doublets and triplets of doublets) occur for the P donor atoms, and two $^{13}C\{^1H\}$ NMR doublets of triplets are seen for the ^{13}CO-enriched carbonyl ligands.



Scheme 6.



Scheme 7.

Table 1
$^{31}P\{^1H\}$ and carbonyl region $^{13}C\{^1H\}$ NMR data for complexes **9**, **9′**, and **9″**[a]

Complex	δP_C	δP_W	$^2J_{PP}$	$\delta^{13}CO$	$^2J_{PcC}$	$^2J_{PwC}$
9	3.945	37.758	47.7			
9′	3.938	37.758	47.8	222.98	21.9	18.9
9″	3.952	37.763	47.6	212.97	15.9	14.1

[a] δ in ppm, J in Hz. Assignment of **9′** and **9″** is arbitrary.

The observation of *syn* and *anti* isomers appears to be the first for a five-coordinate complex. The isomers **9′** and **9″** most likely differ by the angles between the ^{13}C and ^{31}P nuclei [2] caused by the orientation of the Ph group of Cyttp. The occurrence of separate resonances in the $^{31}P\{^{1}H\}$ NMR spectrum for **9**, **9′**, and **9″** is a consequence of slight differences in the shielding of the ^{31}P nuclei by ^{12}C and ^{13}C [23].

The fact that **2′**(O_3SCF_3) and **2″**(O_3SCF_3) yield the same mixture of reduction products indicates that neither carbonyl ligand is lost during the reaction. A pathway involving attack of *n*-BuLi at Ru followed by alkyl migration, and then addition of another *n*-Bu^- to Ru followed by reductive elimination of 5-nonanone, can therefore be excluded. The only reasonable mechanism appears to be a free radical one. It is possible that reduction occurs by two one-electron steps, and that the first step leads to a product that undergoes *syn–anti* isomerization, since the starting **2′** or **2″** exists as a single isomer, most likely *anti* [1,2]. However, it cannot be ruled out that isomerization occurs after the formation of **9′** or **9″**.

Five-coordinate trigonal bipyramidal complexes undergo equatorial and apical ligand scrambling, which may occur by a so-called 2-for-2 (2 equatorial for 2 apical) exchange process, viz., Berry pseudorotation or the "turnstile rotation" [24]. However, we can find no way of applying either of these mechanisms to rationalize *syn–anti* isomerization of **9′/9″**. Nevertheless, another intramolecular pathway appears plausible. The molecular motion effecting this process may be envisaged by viewing one *syn–anti* isomer from the equatorial plane. When the Ru(CO)(^{13}CO) "wedge" is rotated clockwise by 90° about the line passing through P_C and bisecting the angle OC–Ru–^{13}CO, while the Cyttp ligand is rotated counterclockwise by 90°, the other *syn–anti* isomer results. This mechanism differs from both Berry pseudorotation and the "turnstile rotation" in that there is no exchange between equatorial and apical sites.

4. Conclusion

The complex [*cis-mer*-Ru(OSO_2CF_3)($CO)_2$(Cyttp)]$^+$, obtained by carbonylation of the previously prepared [1] *cis-mer*-Ru($OSO_2CF_3)_2$(CO)(Cyttp), undergoes substitution of triflate by various monodentate ligands with high stereospecificity. Its configurationally stable ^{13}C isotopomers [*cis-mer*-Ru(OSO_2CF_3)(CO)(^{13}CO-*trans* to P_C)(Cyttp)]$^+$ and [*cis-mer*-Ru(OSO_2CF_3)(CO)(^{13}CO-*cis* to all P donors)(Cyttp)]$^+$ have been selectively synthesized and used to gain mechanistic insight into reactions with $LiHBEt_3$, NaOMe/CO, and *n*-BuLi. These reactions proceed, respectively, by: (a) substitution of hydride for triflate *without* ligand rearrangement, (b) addition of methoxide to CO *with* ligand rearrangement, and (c) reduction to the same two ruthenium(0) products of each isotopomer of **2**. Results of this study suggest that other, related transition-metal Cyttp complexes may serve as good models for investigations of reaction mechanisms.

Acknowledgements

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