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Comparison of the reactions of $Ru(CO)_2$(triphos) (triphos = etp, ttp and Cyttp) with I_2 and CH_3I

Guochen Jia* and **Devon W. Meek**†
Department of Chemistry, The Ohio State University, 140 West 18th Avenue, Columbus, OH 43210 (U.S.A.)

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Abstract

The products of the reactions of I_2 and CH_3I with $Ru(CO)_2$(triphos) (triphos = etp ($PhP(CH_2CH_2PPh_2)_2$), ttp ($PhP(CH_2CH_2CH_2PPh_2)_2$) and Cyttp ($PhP(CH_2CH_2CH_2PCy_2)_2$)) were characterized by $^{31}P\{^1H\}$, ^1H, $^{13}C\{^1H\}$ NMR and IR spectroscopy, and elemental analyses. The etp complex $Ru(CO)_2$(etp) was prepared by treatment of $Ru_3(CO)_{12}$ with etp in refluxing benzene. *fac*-[$RuX(CO)_2$(etp)]I (X = I, Me) were produced when $Ru(CO)_2$(etp) was treated with I_2 and CH_3I, respectively, either at room temperature or on refluxing. At room temperature, *cis-mer*-[$RuI(CO)_2$(triphos)]I and [$RuMe(CO)_2$(triphos)]I (triphos = ttp and Cyttp) were the products of the reaction of $Ru(CO)_2$(triphos) with I_2 and CH_3I, respectively. The neutral complexes $RuI_2(CO)$(triphos) (triphos = ttp and Cyttp) were synthesized by treatment of $Ru(CO)_2$(triphos) with I_2 in refluxing benzene.

Introduction

Oxidative addition reactions of low valent metal complexes are one of the important methods of preparation of inorganic and organometallic compounds and key features of many catalytically important processes and have been studied extensively [1].

There are a few reports on the oxidative addition reactions of ruthenium carbonyl complexes containing chelating polyphosphines. Additions of X_2 ($X_2 = Cl_2$, Br_2, I_2) [2, 3] to $Ru(CO)_2$(tripod) (tripod = $MeC(CH_2PPh_2)_3$) at room temperature produced initially [$RuX(CO)_2$(tripod)]X, which were converted into $RuX_2(CO)$(tripod) on attempted purification. The complexes [$RuR(CO)_2$(tripod)]$^+$ (R = H, Me, Et, $PhCH_2$, allyl) were produced by treatment of $Ru(CO)_2$(tripod) with anhydrous hydrogen chloride and alkyl halides [3]. The triphosphine complexes *mer*-[$Ru(X)(CO)_2$(Cyttp)]X (X = Br, I), Cyttp = $PhP(CH_2CH_2CH_2PCy_2)_2$, were isolated as the only products from the reactions of $Ru(CO)_2$(Cyttp) with X_2 at room temperature [4]. We herein report the synthesis and spectroscopic properties of a series of ruthenium carbonyl complexes prepared by the reactions of I_2 and CH_3I with $Ru(CO)_2$(triphos) (triphos = etp, ttp and Cyttp).

Experimental

All manipulations were performed at room temperature under an argon atmosphere using standard Schlenk techniques, unless stated otherwise. Solvents were all reagent grade and were distilled over argon from appropriate drying agents prior to use. Solutions were transferred by use of syringes that were flushed with argon before use. Air-sensitive solids were handled and transferred in a Vacuum Atmospheres HE43 inert atmosphere box equipped with a Mo-40 catalyst system. Minute traces of oxygen and water were removed from commercially available argon by passing the gas through two columns packed with hot (180 °C) BASF active copper catalyst and Drierite, respectively.

Iodine (J. T. Baker Co.), etp (Pressure Chemical Co.) and $Ru_3(CO)_{12}$ (Strem Chemical Inc.) were used as purchased. Methyl iodide (EM Science) was distilled over P_2O_5 under an argon atmosphere before use. The complexes $Ru(CO)_2$(ttp), $Ru(CO)_2$(Cyttp)

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*Author to whom correspondence should be addressed at the Department of Chemistry, University of Toronto, Toronto, Ont., M5S 1A1, Canada.

†Deceased December 7, 1988.

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and [RuI(CO)$_2$(Cyttp)]I were prepared according to literature methods [4].

Infrared spectra were recorded on a Perkin-Elmer 283B grating spectrophotometer from 4000 to 200 cm^{-1}, as pressed potassium bromide pellets, Nujol mulls, or in solution. Spectra were calibrated against the sharp 1601 cm^{-1} peak of polystyrene film. A Bruker AM-250 spectrometer was used to obtain proton (250.13 MHz), phosphorus-31 (101.25 MHz) and carbon-13 (62.9 MHz) NMR spectra in 5 mm tubes. Residual solvent proton or carbon-13 resonances were used as internal standards for the ^{1}H or ^{13}C NMR spectra. Phosphorus chemical shifts were determined relative to 85% H_3PO_4 as an external standard. ^{31}P{^{1}H} NMR and selected IR spectroscopic data for the ruthenium carbonyl complexes are collected in Table 1, and selected ^{13}C{^{1}H} and ^{1}H NMR data in Table 2.

Conductivity data were obtained on *c.* 10^{-3} M nitromethane solutions with a Lab Line unbreakable-type conductivity cell, Catalog No. 11200. An Industrial Instruments Inc. conductivity bridge (model RC16B2) was used to determine the resistance of solutions at 1000 Hz. In the experimental section, the molar conductance values Λ_M have the unit ohm^{-1} c m^2 mol^{-1}. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

Ru(CO)$_2$(etp)

A solution of 0.40 g of $Ru_3(CO)_{12}$ (1.9 mmol of Ru) and 1.11 g of etp (2.07 mmol) in 70 ml of benzene was refluxed for 18 h to give a light yellow–orange solution. The solvent was removed under vacuum until some yellow solids were formed (*c.* 2 ml) and then 50 ml of hexane was added to the reaction mixture to give a yellow solid. The solid was collected on a filter frit, washed with hexane, and dried under vacuum overnight. Yield: 0.91 g, 70%. *Anal.* Calc. for $C_{36}H_{33}O_2P_3Ru$: C, 62.52; H, 4.81; P, 13.43. Found: C, 62.42; H, 5.00; P. 13.26%.

[RuI(CO)$_2$(etp)]I

A solution of 0.0550 g of iodine (0.217 mmol) in 20 ml of benzene was added slowly to a solution of 0.15 g of Ru(CO)$_2$(etp) (0.22 mmol) in 10 ml of benzene. The color of iodine disappeared very quickly and the reaction mixture became cloudy immediately upon addition of iodine. After stirring for 30 min the resulting pale-yellow solid was collected on a filter frit, washed with benzene and ether, and dried under vacuum overnight. Yield: 0.18 g, 88%. *Anal.* Calc. for $C_{36}H_{33}I_2O_2P_3Ru$: C, 45.74; H, 3.52; I, 26.84. Found: C, 45.50; H, 3.71; I, 26.67%. $\Lambda_M = 94$.

[RuMe(CO)$_2$(etp)]I

A mixture of 0.20 g of Ru(CO)$_2$(etp) (0.29 mmol) and 0.5 ml of MeI (8 mmol) in 20 ml of benzene was stirred for 6 h to give a white solid. The solid was collected on a filter frit, washed with benzene and ether, and dried under vacuum overnight. Yield: 0.19 g, 79%. *Anal.* Calc. for $C_{37}H_{36}IO_2P_3Ru$: C, 53.31; H, 4.36; I, 15.22. Found: C, 53.35; H, 4.29; I, 15.36%. $\Lambda_M = 94$.

[RuI(CO)$_2$(ttp)]I

A solution of 0.0529 g of iodine (0.208 mmol) in 20 ml of benzene was added slowly to a solution of

TABLE 1. ^{31}P NMR[a] and selected infrared[b] data for the ruthenium carbonyl complexes

Compound	^{31}P NMR			Solvent	IR (cm^{-1}) ν(CO)
	$\delta(P_1)$	$\delta(P_2)$	$J(P_1P_2)$		
Ru(CO)$_2$(etp)	109.4	76.5	32.9	C_6H_6	1930, 1870
Ru(CO$_2$)(ttp)[c]	−0.1	35.0	50	C_6H_6	1900, 1845
Ru(CO)$_2$(Cyttp)[c]	4.7	38.6	48	C_6H_6	1880, 1820
[RuI(CO)$_2$(etp)]I	79.1	57.5, 45.5	[d]	acetone	2045, 2000
[RuI(CO)$_2$(ttp)]I	−18.9	−5.1	37.8	CH_3NO_2	2040, 2010
[RuI(CO)$_2$(Cyttp)]I[c]	−18.0	2.7	34	acetone	2045, 1985
RuI$_2$(CO)(ttp)	8.1	−8.8	31.8	CH_2Cl_2	1980
RuI$_2$(CO)(Cyttp)	7.8	−8.4	30.5	CH_2Cl_2	1950
[RuMe(CO)$_2$(etp)]I	84.3	59.4, 45.9	[e]	acetone	2015, 1975
trans-[RuMe(CO)$_2$(ttp)]I	−8.8	15.1	28.6	CH_3NO_2	1980
trans-[RuMe(CO)$_2$(Cyttp)]I	−8.6	13.1	24.3	CH_3NO_2	1970
cis-[RuMe(CO)$_2$(Cyttp)]I	−10.8	10.8	37.8	CH_3NO_2	2010, 1965
RuMeI(CO)(ttp)	−13.5	16.1	44.9	CH_2Cl_2	1925

[a] ^{31}P chemical shifts are in ppm with respect to external 85% H_3PO_4 (δ 0.0); positive values are downfield; coupling constants are in Hz; P_1 is the central phosphorus atom and P_2 the two terminal phosphorus atoms in the triphosphine ligand. [b] Spectra were obtained in KBr disks. [c] From ref. 4. [d] $J(P_1P_2) = 9.8$ Hz, $J(P_1P'_2) = 17.1$ Hz, $J(P_2P'_2) = 21.0$ Hz. [e] $J(P_1P_2) = 6$ Hz, $J(P_1P'_2) = 21$ Hz, $J(P_2P'_2) = 18$ Hz.

TABLE 2. ^{13}C and ^{1}H NMR data for the ruthenium carbonyl complexes[a]

Compound	^{13}C NMR		^{1}H NMR δ(Me)
	δ(CO)	δ(Me)	
$[RuI(CO)_2(ttp)]I$	192.1(q; $J=10$ Hz) 188.6(dt; $J=86.9$, 10.5 Hz)		
$[RuI(CO)_2(Cyttp)]I$[b]	194.9(q; $J=11.2$ Hz) 193.8(dt; $J=87.4$, 10.5 Hz)		
$RuI_2(CO)(ttp)$	199.6(q; $J=10.0$ Hz)		
$RuI_2(CO)(Cyttp)$	201.2(q; $J=9.2$ Hz)		
$[RuMe(CO)_2(etp)]I$	197.9(ddd; $J=82.0$, 12.9, 7.4 Hz) 200.9(ddd; $J=80.5$, 13.4, 7.3 Hz)	−18.8(dt; $J=34.8$, 7.8 Hz)	−0.65(td; $J=6.6$, 3.0 Hz)[c]
trans-$[RuMe(CO)_2(ttp)]I$	200.5(td; $J=13.1$, 7.7 Hz) 201.1(td; $J=13.5$, 8.5 Hz)	−15.1(dt; $J=27.9$, 6.1 Hz)	−0.38(td; $J=5.5$, 2.9 Hz)
trans-$[RuMe(CO)_2(Cyttp)]I$[b]	203.6(q; $J=9$ Hz) 205.4(q; $J=9$ Hz)	−23.0(dt; $J=28.6$, 7.2 Hz)	−0.10(td; $J=5.1$, 2.8 Hz)
cis-$[RuMe(CO)_2(Cyttp)I$		−10.2(q; $J=7.4$ Hz)	−0.52(q, $J=6$ Hz)
$RuMeI(CO)(ttp)$	205.8(dt; $J=87.9$, 14.7 Hz)	−1.77(q; $J=6.4$ Hz)	

[a] Spectra were obtained in CD_2Cl_2 except where indicated. Chemical shifts are in ppm with respect to Me_4Si; positive values are downfield. d = doublet, q = quartet, t = triplet. [b] In CD_3NO_2 solution. [c] In CD_3CN.

0.15 g of $Ru(CO)_2(ttp)$ (0.21 mmol) in 10 ml of benzene. After stirring for *c.* 30 min the resulting light-yellow solid was collected on a filter frit, washed with benzene and ether, and dried under vacuum overnight. Yield: 0.18 g, 90%. *Anal.* Calc. for $C_{38}H_{37}I_2O_2P_3Ru$: C, 46.88; H, 3.86; I, 26.07. Found: C, 46.07; H, 3.96; I, 25.69%. $\Lambda_M = 98$.

$RuI_2(CO)(ttp)$

A solution of 0.0352 g of iodine (0.139 mmol) in 15 ml of benzene was added slowly to a boiling solution of 0.10 g of $Ru(CO)_2(ttp)$ (0.14 mmol) in 10 ml of benzene. The color of iodine disappeared and a yellow solid formed immediately upon addition of iodine. After refluxing for 2 h, the initially formed yellow solid disappeared and a yellow solution was obtained. The volume of the reaction mixture was reduced until the solution became cl6udy (*c.* 2 ml), and then 20 ml of ether was added to give a yellow solid. The solid was collected on a filter frit, washed with ether, and dried under vacuum overnight. Yield: 0.11 g, 84%. *Anal.* Calc. for $C_{37}H_{37}I_2OP_3Ru$: C, 47.01; H, 3.95; I, 26.84. Found: C, 46.97; H, 4.02; I, 26.59%.

$[RuMe(CO)_2(ttp)]I$

A mixture of 0.15 g of $Ru(CO)_2(ttp)$ (0.21 mmol) and 0.5 ml of MeI (8 mmol) in 15 ml of benzene was stirred for 6 h to give a white solid. The solid was then collected on a filter frit, washed with benzene and ether, and dried under vacuum overnight. Yield: 0.16 g, 89%. *Anal.* Calc. for $C_{39}H_{40}IO_2P_3Ru$: C, 54.37; H, 4.68; I, 14.70. Found: C, 54.20; H, 4.65; I, 14.59%. $\Lambda_M = 96$.

$RuMe(I)(CO)(ttp)$

A mixture of 0.15 g of $Ru(CO)_2(ttp)$ (0.21 mmol) and 0.5 ml of MeI (8 mmol) in 20 ml of benzene was refluxed for 2 h to give a yellow solution. The volume of the reaction mixture was reduced until the solution became cloudy (*c.* 2 ml), and then 20 ml of ether was added to give a light yellow solid. The solid was collected on a filter frit, washed with ether, and dried under vacuum overnight. Yield: 0.13 g, 75%. *Anal.* Calc. for $C_{38}H_{40}IOP_3Ru$: C, 54.75; H, 4.83; I, 15.22. Found: C, 54.41; H, 4.64; I, 15.43%.

$RuI_2(CO)(Cyttp)$

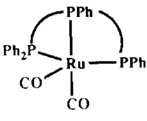
A solution of 0.0342 g of iodine (0.133 mmol) in 20 ml of benzene was added slowly to a boiling solution of 0.10 g of $Ru(CO)_2(Cyttp)$ in 10 ml of benzene. The color of iodine disappeared immediately and the reaction mixture became cloudy in a few minutes addition of iodine. A yellow solution was obtained after refluxing overnight. The volume of the reaction mixture was reduced to *c.* 1 ml, and 20 ml of ether was added to give a bright yellow solid. The solid was collected on a filter frit, washed with ether, and dried under vacuum overnight. Yield: 0.10 g, 77%. *Anal.* Calc. for $C_{37}H_{61}I_2OP_3Ru$: C, 45.83; H, 6.34; I, 26.17. Found: C, 45.74; H, 6.39; I, 26.23%.

Results and discussion

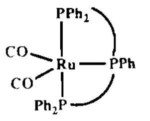
Preparation and structure of $Ru(CO)_2(etp)$

Like ttp, Cyttp and tripod, the triphosphine etp also forms $Ru(CO)_2(etp$ (**1**) directly from $Ru_3(CO)_{12}$.

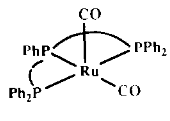
The complex $Ru(CO)_2(etp)$ displays infrared bands at 1930 and 1870 cm^{-1} with similar intensity, which implies that the two carbonyl groups are *cis* to each other [5]. The ^{31}P NMR spectrum of $Ru(CO)_2(etp)$ in benzene exhibits a doublet at 76.5 ppm for the two terminal phosphorus atoms and a triplet at 109.4 ppm ($J(PP) = 32.9$ Hz) for the central phosphorus atom. The spectroscopic data are consistent with the proposed structure **1A**, **1B** or **1C** as shown below. Although **1B** and **1C** cannot be excluded, the TBP structure **1A** is preferred for the d^8 Ru(0) complex, based on the following arguments. It has been reported that trigonal bipyramidal geometry is more stable than square pyramidal geometry for high-spin d^4, d^9 and low-spin d^8 configurations [6]. The isoelectronic complexes $[Co(CO)(L)(etp)]X$ ($L = CO$, $P(OMe)_3$, PPh_2H, PPh_2Me, PEt_3) are trigonal bipyramidal with the equatorial positions occupied by a carbonyl ligand and the two terminal phosphorus atoms of the triphosphine, i.e. like structure **1A** [7]. Facial etp ruthenium complexes are known, for example, $(etp)ClRu(\mu\text{-}Cl)_2RuCl(etp)$ [8]. In addition, the products of the reactions of $Ru(CO)_2(etp)$ with I_2 and MeI are all facial compounds (see below).



1A



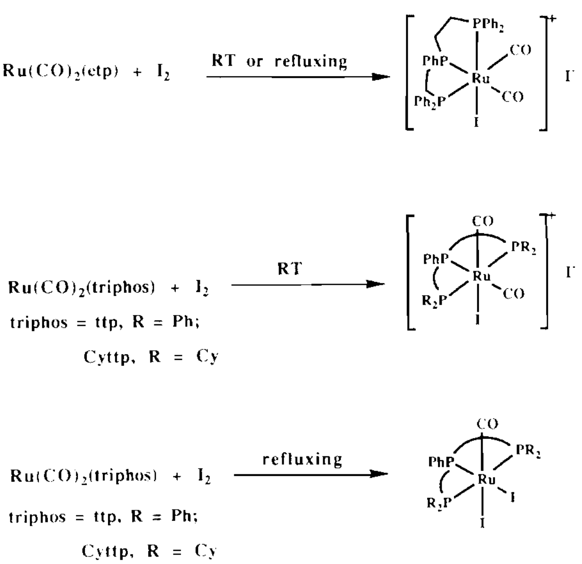
1B



1C

Reactions of iodine

The reactions of I_2 with $Ru(CO)_2(triphos)$ are summarized in Scheme 1. It has been reported that treatment of $Ru(CO)_2(Cyttp)$ with molecular halogens X_2 (e.g. Br_2, I_2) produced *cis-mer*-$[RuX(CO)_2(Cyttp)]X$ at room temperature [4], while treatment of $Ru(CO)_2(tripod)$ with X_2 (e.g. Cl_2, Br_2, I_2) [2, 3] gives initially $[RuX(CO)_2(tripod)]X$, which were readily converted into neutral complexes $RuX_2(CO)(tripod)$. Treatment of $Ru(CO)_2(etp)$ and $Ru(CO)_2(ttp)$ with one equivalent of iodine at room temperature also gives similar compounds $[RuI(CO)_2(etp)]I$ (**2**) and $[RuI(CO)_2(ttp)]I$ (**3**), respectively. It was also noted that intractable products were obtained when excess iodine was employed.



Scheme 1. Reactions of $Ru(CO)_2(triphos)$ (triphos = etp, ttp, and Cyttp) with I_2 in benzene.

The spectroscopic data of $[RuI(CO)_2(etp)]I$ suggest that $[RuI(CO)_2(etp)]I$ has the structure shown in Scheme 1. Its ^{31}P NMR spectrum displays three doublet of doublets resonances. The structure proposed is the only one fitting the ^{31}P NMR data. The most downfield signal at 79.1 ppm is assigned to the central PPh group since it is the bridgehead of two five-membered rings, thus a very low field chemical shift is expected [9]. The resonances at 57.5 and 45.5 ppm are assigned to the PPh_2 group *trans* to iodide and the one *trans* to a carbonyl, respectively, based on the *trans* influence of iodide and carbonyl on phosphorus chemical shifts [9]. The infrared spectrum shows two equally strong carbonyl absorptions characteristic of *cis* carbonyls [5].

The spectroscopic data of $[RuI(CO)_2(ttp))]I$ are consistent with the structure shown in Scheme 1, which is similar to that of $[RuI(CO)_2(Cyttp)]I$ [4]. The infrared spectrum of $[RuI(CO)_2(ttp)]I$ shows two equally strong carbonyl absorptions (at 2040 and 2010 cm^{-1}) characteristic of *cis* carbonyls [5]. Its ^{31}P NMR spectrum shows a doublet at -5.1 ppm for the two terminal phosphorus atoms and a triplet at -18.9 ppm ($J(PP) = 37.8$ Hz) for the central phosphorus atom. The pattern indicates that the triphosphine is meridional around ruthenium and that the central phosphorus atom is *trans* to a carbonyl rather than the iodide [9]. Consistent with the structure, in the ^{13}C NMR spectrum, the resonance for the carbonyl *trans* to the central phosphorus atom was observed at 188.6 ppm (dt; $J(PC) = 86.9$, 10.5 Hz) and that for the carbonyl *cis* to the three phosphorus atoms at 192.1 ppm (q, $J(PC) = 10$ Hz). The *cis* and *trans* ^{31}P–^{13}CO coupling constants are comparable to those observed in similar ruthenium carbonyl complexes [10].

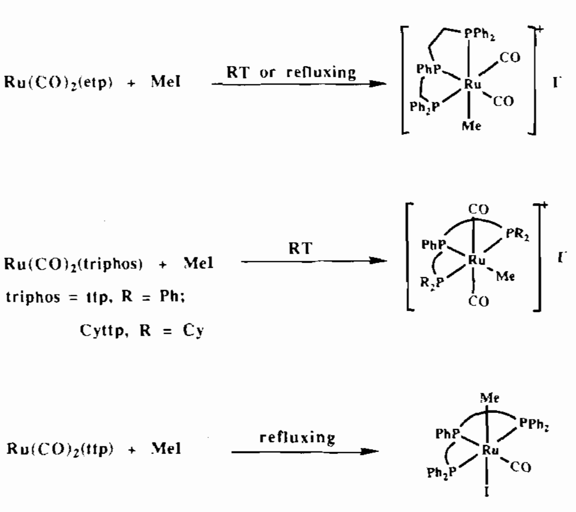
The neutral complex $RuI_2(CO)(ttp)$ (**4**) was formed when $Ru(CO)_2(ttp)$ was treated with one equivalent of iodine in boiling benzene and refluxed for 2 h. Similarly $RuI_2(CO)(Cyttp)$ (**5**) was produced when a mixture of $Ru(CO)_2(Cyttp)$ and one equivalent of iodine was refluxed in benzene overnight. The neutral complexes were formed via the intermediates

$[RuI(CO)_2(triphos)]I$ by displacement of a carbonyl group with the iodide anion as the formation and disappearance of a yellow solid of $[RuI(CO)_2(triphos)]I$ were observed. Interestingly, no detectable amount of $RuI_2(CO)(etp)$ was formed when a mixture of $Ru(CO)_2(etp)$ and one equivalent of iodine in benzene was refluxed for 14 h; only $[RuI(CO)_2(etp)]I$ was produced. In contrast, it has been reported that conversion of $[RuX(CO)_2(tripod)]X$ (X = Cl, Br, I) to $RuX_2(CO)(tripod)$ occurred readily [2, 3]. The difference in the stability of $[RuI(CO)_2(triphos)]I$ seems related to the Ru–CO bond strength. For example, carbonyl absorptions were observed at 2078 and 2040 cm^{-1} in $[RuI(CO)_2(tripod)]PF_6$ [3] while the carbonyl absorptions were observed below 2045 cm^{-1} in $[RuI(CO)_2(triphos)]I$ (triphos = Cyttp, ttp, etp). The lower CO frequencies imply the stronger Ru–CO bond present in the latter complexes.

The complexes $RuI_2(CO)(triphos)$ (triphos = ttp, Cyttp) have very similar properties and therefore similar structures. Both $RuI_2(CO)(triphos)$ (triphos = ttp, Cyttp) are insoluble in polar solvents such as acetone and acetonitrile, but soluble in benzene and dichloromethane. In their ^{13}C NMR spectra, the carbonyl resonances were observed at 199.6 ppm (q, $J(PC) = 10.0$ Hz) for $RuI_2(CO)(ttp)$ and 201.2 ppm (q, $J(PC) = 9.2$ Hz) for $RuI_2(CO)(Cyttp)$. The magnitude of the coupling constants $^2J(^{31}P–^{13}CO)$ and the pattern of the carbonyl resonances support that the carbonyl is *cis* to the three phosphorus atoms of the triphosphine in both complexes. Thus the triphosphines are meridional around ruthenium and the iodide ligands are *cis* to each other in the diiodo complexes. The ^{31}P NMR spectra of both complexes show an A_2B pattern and the phosphorus chemical shift of the central PPh group is located downfield from that of the terminal PR_2 groups, which also suggest that the triphosphines are meridional around ruthenium and that an iodide rather than the CO is *trans* to the central PPh group [9].

Reactions of MeI

The reactions of MeI with $Ru(CO)_2(triphos)$ are summarized in Scheme 2. The reactivity of $Ru(CO)_2(triphos)$ (triphos = etp, ttp, Cyttp) toward MeI at room temperature is very similar. Thus, $[RuMe(CO)_2(triphos)]I$ (triphos = etp, **6**; ttp, **7**; Cyttp, **8**) were obtained when $Ru(CO)_2(triphos)$ were treated with MeI at room temperature in benzene. However, the structures of the products are dependent on the triphosphine.

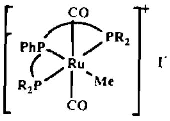


Scheme 2. Reactions of $Ru(CO)_2(triphos)$ (triphos = etp, ttp, and Cyttp) with MeI in benzene.

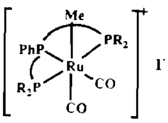
The structure of $[RuMe(CO)_2(etp)]I$ is similar to that of $[RuI(CO)_2(etp)]I$. The infrared spectrum of $[RuMe(CO)_2(etp)]I$ displays two equally strong carbonyl absorptions at 2015 and 1975 cm^{-1} indicating that the two carbonyls are *cis* to each other [5]. Its ^{31}P NMR spectrum shows three doublet of doublets resonances; thus the triphosphine is facially bonded to ruthenium. The resonances at 84.3, 59.4 and 45.9 ppm are assigned to the central PPh group, the PPh_2 group *trans* to the methyl and the PPh_2 group *trans* to a carbonyl, respectively, by analogy to the spectral assignments of $[RuI(CO)_2(etp)]I$. the Ru–Me resonance in the ^1H NMR spectrum was observed at -0.65 ppm (td, $J(PH) = 6.6$ (*cis*), 3.0 (*trans*) Hz). The chemical shift is comparable with the value -0.41 ppm for the Ru–Me in $[RuMe(CO)(PMe_2Ph)(tripod)]PF_6$ [10]. The trend that *cis* coupling between phosphorus and methyl protons is larger than *trans* coupling is consistent with other observations on similar ruthenium complexes [3, 10]. In the ^{13}C NMR spectrum, the Ru–Me resonance appeared at -18.8 ppm (dt, $J(PC) = 34.8$, 7.8 Hz). The resonances at 197.9 and 200.9 ppm assignable to the two carbonyls were also observed.

Although the structure of $[RuMe(CO)_2(etp)]I$ is similar to that of $[RuI(CO)_2(etp)]I$, the structures of $[RuMe(CO)_2(ttp)]I$ and $[RuI(CO)_2(ttp)]I$ are different. The two carbonyls are *trans* to each other in $[RuMe(CO)_2(ttp)]I$ (the carbonyls are *cis* to each other in $[RuI(CO)_2(ttp)]I$). The infrared spectrum of $[RuMe(CO)_2(ttp)]I$ shows only one strong carbonyl absorption at 1980 cm^{-1}, which is consistent with the two carbonyls essentially *trans* to each other [5]. In its ^{13}C NMR spectrum the resonances at 200.5 (td; $J(PC) = 13.1$, 7.7 Hz) and 201.1 (td; $J(PC) = 13.5$, 8.5 Hz) ppm assignable to the two carbonyls were observed. The two carbonyls are slightly different from each other owing to the fixed orientation of the phenyl group on the central phosphorus atom of the triphosphine. The infrared and ^{13}C NMR data suggest that both carbonyls are *cis* to the three phosphorus atoms of the triphosphine and the triphosphine is meridional around ruthenium. The Ru–Me resonance was observed at -15.1 ppm (dt, $J(PC) = 27.9, 6.1$ Hz) in the ^{13}C NMR spectrum. The Ru–Me resonance in the ^1H NMR spectrum was observed at -0.38 ppm (td, $J(PH) = 5.5, 2.9$ Hz); again *cis* $^3J(PH)$ coupling is larger than the *trans* coupling. Its ^{31}P NMR spectrum shows A_2B pattern and the phosphorus chemical shift of the central PPh group is located upfield from that of the terminal PPh_2 groups; which is similar to that of *cis*-$[RuI(CO)_2(ttp)]I$.

Treatment of $Ru(CO)_2(Cyttp)$ with MeI at room temperature produced a white solid. The white solid isolated from the reaction consists of predominantly isomer **8A** and trace amount of isomer **8B** (structures shown below). When solutions of the white solid in dichloromethane, nitromethane, or acetonitrile were kept at room temperature, the amount of isomer **8A** decreased, and the amount of isomer **8B** increased. However, isomer **8A** could not be converted into isomer **8B** completely (e.g isomer **8A** was still the major species in CD_3NO_2 solution after the solution was kept at room temperature for nine days). It is interesting to note that only one isomer was observed for the analogous compound $[RuMe(CO)_2(ttp)]I$.



8A



8B

The ^{31}P, IR, ^1H and ^{13}C NMR data for **8A** are very similar to those observed for $[RuMe(CO)_2(ttp)]I$ (see Tables 1 and 2), thus a structure similar to that of $[RuMe(CO)_2(ttp)]I$ is assigned to **8A** of $[RuMe(CO)_2(Cyttp)]I$ in which two CO are *trans* to each other. Isomer **8B** is also a meridional compound, but the two carbonyls are *cis* to each other. In the ^{13}C NMR spectrum, the Ru–Me resonance was observed at -10.2 ppm as a quartet with $^2J(PC) = 7.2$ Hz, which suggests that the methyl group is *cis* to the three phosphorus atoms of the triphosphine and that the triphosphine is meridional around ruthenium. In the ^{31}P NMR spectrum, a doublet at 10.8 ppm, assignable to the two PCy_2 groups, and a triplet at -10.8 ppm, assignable to the central PPh group, were observed. The infrared bands at 2010 and 1965 cm^{-1} were assigned to the carbonyl absorptions for the isomer. The Ru–Me resonance in the ^1H NMR spectrum in CD_2Cl_2 was observed at -0.52 ppm (q, $^3J(PH) = 6$ Hz).

Different products were obtained when the reactions of MeI were carried out in refluxing benzene. The neutral complex RuMe(I)(CO)(ttp) could be isolate by treatment of $Ru(CO)_2(ttp)$ with MeI in refluxing benzene [11]. However, $[RuMe(CO)_2(etp)]I$ was isolated even when a mixture of $Ru(CO)_2(etp)$ and MeI in benzene was refluxed for 22 h. The reaction of $Ru(CO)_2(Cyttp)$ with MeI in refluxing benzene resulted in a complicated mixture as indicated by the *in situ* ^{31}P NMR spectrum. Similarly, a complicated mixture was also obtained when the isolated $[RuMe(CO)_2(Cyttp)]I$ was refluxed in benzene for several hours. The relatively easy conversion of $[RuMe(CO)_2(ttp)]I$ to the neutral complex Ru(Me)(I)(CO)(ttp) compared with the difficulty of conversion of $[RuMe(CO)_2(etp)]I$ to the corresponding neutral compound is probably related to the fact that the two carbonyls are *trans* to each other in $[RuMe(CO)_2(ttp)]I$ whereas the two carbonyls are *trans* to phosphorus atoms in $[RuMe(CO)_2(etp)]I$. Thus the two carbonyls in $[RuMe(CO)_2(ttp)]I$ are electronically more unfavorable owing to the presence of *trans* strong π-acceptor carbonyls compared with $[RuMe(CO)_2(etp)]I$.

This study shows that the reactivity of $Ru(CO)_2(triphos)$ (triphos = etp, ttp, Cyttp) toward I_2 and MeI at room temperature is similar except that the stereochemistry of the reaction products are different. The triphosphines $PhP(CH_2CH_2CH_2PR_2)_2$ (R = Ph, Cy) prefer meridional arrangement whereas $PhP(CH_2CH_2PPh_2)_2$ prefers a facial arrangement in an octahedral ruthenium complex. Such structural preference has been noted in other metal (such as cobalt) systems and has been attributed to a decrease in chelate bite angle of the etp ligand [7]. Treatment of $Ru(CO)_2(triphos)$ (triphos = ttp and Cyttp) with I_2 at room temperature gives *cis-mer*-$[RuI(CO)_2(triphos)]I$ whereas with MeI gives *trans-mer*-$[RuMe(CO)_2(triphos)]I$. Different products were obtained when the reactions were carried out in refluxing benzene.

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References

1 (a) J. D. Atwood, *Inorganic and Organometallic Reaction Mechanism*, Brooks/Cole Publishing Co., Monterey,CA,

1985; (b) P. R. Collman and L. S. Hegedus, *Principles and Applications of Organotransition Metal Complexes,* University Science Books, Mill Valley, CA, 1980.

2 W. O. Siegl, S. J. Lapporte and J. P. Collman, *Inorg. Chem., 12* (1973) 674.

3 S. I. Hommeltoft and M. C. Baird, *Organometallics, 5* (1986) 190.

4 J. B. Letts, T. J. Mazanec and D. W. Meek, *Organometallics, 2* (1983) 695.

5 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry,* Wiley-Interscience, New York, 4th edn., 1980, pp. 1073–1076.

6 B. F. Hoskins and F. D. Whillans, *Coord. Chem. Rev., 9* (1972) 365.

7 D. L. Dubois and D. W. Meek, *Inorg. Chem., 15* (1976) 3076.

8 R. B. King, P. N. Kapoor and R. N. Kapoor, *Inorg. Chem., 10* (1971) 1841.

9 D. W. Meek and T. J. Mazanec, *Acc. Chem. Res., 14* (1981) 266.

10 S. I. Hommeltoft, A. D. Cameron, T. A. Shackleton, M. E. Fraser, S. Fortier and M. C. Baird, *Organometallics, 5* (1986) 1380.

11 T. J. Mazanec, *Ph.D. Dissertation,* The Ohio State University, 1978.