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Preliminary communication

PREPARATION OF $Ru(CO)_3(PMe_3)MeI$ AND ITS ACETYL DERIVATIVES

GIUSEPPE CARDACI
Department of Chemistry, University of Perugia, 06100 Perugia (Italy)

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Summary

$[Ru(CO)_4PMe_3]$ reacts with MeI to give *fac*-$[Ru(CO)_3(PMe_3)(Me)I]$. The latter reacts with PMe_3 to give a mixture of the three isomers of *cis*-bis(trimethylphosphine)-*cis*-dicarbonyl acetyl iodide $[Ru(CO)_2(PMe_3)_2(COMe)I]$. Decarbonylation of the mixture gives only the *trans*-bis(trimethylphosphine)-*cis*-dicarbonyl methyl iodide complex $[Ru(CO)_2(PMe_3)_2MeI]$, which was also prepared by oxidative addition of MeI to $[Ru(CO)_3(PMe_3)_2]$.

Alkyl and acyl complexes of ruthenium are intermediates in many catalytic reactions [1], and study of their reactions is thus important to provide clarification of the catalytic mechanisms. In attempted preparations of such species good results have been obtained in the preparation of complexes of the type $[Ru(CO)_2L_2RX]$ by oxidative addition of alkyl halides to trisubstituted derivatives of $[Ru(CO)_5]$ [2] or by electrophilic removal of halide ligands from $[Ru(CO)_2L_2X_2]$ [3] by HgR_2 or SnR_4. No preparations have been reported up to now of the tricarbonyl derivatives $[Ru(CO)_3LRX]$, which should be more reactive than the dicarbonyl derivatives in the catalytic processes.

We describe here the preparation of such ruthenium derivatives and their reactions with carbon monoxide and other nucleophilic ligands. By taking advantage of the basicity and bulk of PMe_3 we have improved the oxidative addition of alkyl iodide to the monosubstituted derivatives of ruthenium $[Ru(CO)_4PMe_3]$. Treatment of $[Ru_3(CO)_{12}]$ with PMe_3 in ethyl ether at room temperature gave a mixture of $[Ru(CO)_4PMe_3]$, $[Ru(CO)_3(PMe_3)_2]$, and $[Ru(CO)_3PMe_3]_3$; $[Ru(CO)_3(PMe_3)_2]$ [4] and $[Ru(CO)_3PMe_3]_3$ [5] have been made previously by other routes. $[Ru(CO)_4PMe_3]$ (ν(CO) 2058.0(s); 1981.5(s); 1944.5(vs) cm^{-1} in ethyl ether) was separated from the mixture by fractional sublimation; $[Ru(CO_3)PMe_3]_3$ is not volatile and remains as a residue whereas $[Ru(CO)_4PMe_3]$ sublimes at room temperature and $[Ru(CO)_3(PMe_3)_2]$ (ν(CO) 1889.5 cm^{-1} in ethyl ether) at 60 °C. When $[Ru(CO)_4PMe_3]$ was treated with CH_3I at 0 °C a mixture of $[Ru(CO)_3(PMe_3)MeI]$ (**1**) and $[Ru(CO)_3(PMe_3)(COMe)I]$ (**2**) was obtained. The equilibrium is

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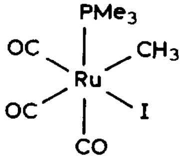
very easily shifted towards **1** by bubbling nitrogen through the solution. The light yellow **1** was crystallized from CH_2Cl_2/n-hexane. Analysis. Found: C, 20.95; H, 2.90. $C_7H_{12}IO_3PRu$ calcd.: C, 20.86; H, 3.00%. ν(CO) 2095.5(s), 2041.0(s), 1999.5(s) cm^{-1} in n-hexane; ^1H NMR spectrum in CD_2Cl_2: $\tau(CH_3)$ 9.54 ppm (d) (J(P–CH_3) 7.5 Hz); $\tau(PMe_3)$ 8.24 ppm (d) (J(P–Me) 9.6 Hz). The number and relative intensities of the CO stretching vibrations indicate a facial structure [6], and this is consistent with the ^1H NMR spectrum [7]. **1** reacts very rapidly with CO to give $[Ru(CO)_3PMe_3(COCH_3)I]$ (**2**); at 1 atm of CO the reaction is incomplete. In n-hexane eight CO stretchings frequencies (ν(CO) 2116.5; 2095.5; 2048.5; 2031.0; 2014.5; 1987.0; 1976.5; 1947.5 cm^{-1}) and a broad $COCH_3$ stretch at 1635 cm^{-1} are observed, indicating the presence of a mixture of geometrical isomers of acetyl complexes. Their number and structures have not yet been ascertained.



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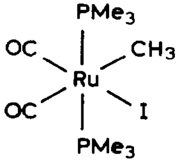

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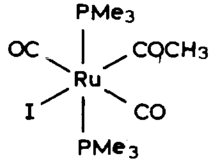

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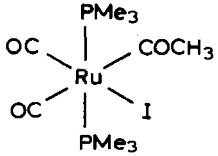

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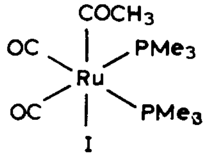

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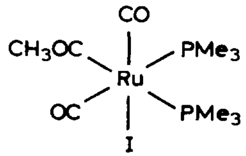

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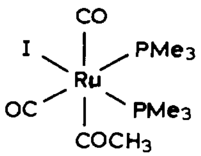

(8)

1 reacts at room temperature with phosphine ligands (PMe_3, PMe_2Ph, etc.). With L = PMe_3 in ethyl ether the reaction was instantaneous, and the pale-yellow product A was crystallized from CH_2Cl_2/n-hexane: Analysis. Found: C, 25.20; H, 4.50. $C_{10}H_{21}IO_3P_2Ru$ calcd.: C, 25.06; H, 4.42%. ν(CO) 2039.5(s), 1975.0(s), $\nu(COCH_3)$ 1618.0(m) cm^{-1} in n-hexane; ^1H NMR spectrum (CD_2Cl_2): $\tau(COCH_3)$: three singlets at 7.24, 7.66 and 7.87 ppm with relative intensity 1/1.3/1.7 attributed to the acetyl groups of three geometrical isomers. In all these isomers the two PMe_3 ligands are in the *cis*-position, as was shown by comparing the data for the A complexes with those for authentic ruthenium complex having the PMe_3 groups in the *trans* position. *trans*-Isomer $[Ru(CO)_2(PMe_3)_2(COCH_3)I]$ was prepared by the reaction of $[Ru(CO)_3(PMe_3)_2]$ with CH_3I at 0 °C; a mixture of *cis,trans*-$[Ru(CO)_2(PMe_3)_2CH_3I]$. (**3**) and *trans,trans*-$[Ru(CO)_2(PMe_3)_2(COCH_3)I]$ (**4**) was immediately obtained. The mixture was readily decarbonylated at room temperature in n-hexane, and complex **3** was obtained as a bright yellow solid by crystallization from n-hexane: Analysis. Found: C, 24.3; H, 4.50. $C_9H_{21}IO_2P_2Ru$ calcd.: C, 23.96; H, 4.69%. ν(CO) 2022.5(s); 1955.5(s) cm^{-1} in n-hexane; ^1H NMR spectrum (CD_2Cl_2): $\tau(CH_3)$ 10.03 ppm (t) (J(P–CH_3) 8.1 Hz); $\tau(PMe_3)$ 8.39 ppm (t) (J(P–Me) 3.8 Hz). **3** reacts with CO in the way described by Mawby for similar complexes [8], to form the *cis*-acetyl complex **5** *cis,trans*-$[Ru(CO)_2(PMe_3)_2(COCH_3)I]$ (ν(CO) 2037.0(s); 1978.0(s) cm^{-1}; $\nu(COCH_3)$ 1613(m) cm^{-1} in n-hexane). Complex **5** isomerizes to complex **4**, which was crystallized as a yellow solid from CH_2Cl_2/n-hexane: Analysis. Found: C, 25.20; H, 4.60. $C_{10}H_{21}IO_3P_2Ru$ calcd.: C, 25.06; H, 4.42%. ν(CO) 2080.0(vw), 1987.5(vs) cm^{-1}; $\nu(COCH_3)$ 1610.5(m) cm^{-1} in n-hexane; ^1H NMR spectrum (CD_2Cl_2): $\tau(COCH_3)$ 7.70 ppm (s); $\tau(PMe_3)$ 8.32 ppm (t) (J(P–Me) 3.8 Hz). The IR and ^1H NMR spectra of **4** and its chemical behaviour rule out its presence in the mixture of complexes **A**: the similar intensities of the CO stretchings frequencies of **A** indicate a *cis* arrangement for the two CO ligands. We therefore assign the structures **6**, **7** and **8** to the three isomers of the **A** mixture. This mixture can be decarbonylated in n-hexane at 60–70 °C by nitrogen bubbling to leave only the methyl complex **3**.

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