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Preliminary communication

TRICHLOROSILYL DERIVATIVES OF THE IRON TRIAD CARBONYLS

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Summary

The reaction of *cis*-$Ru(CO)_4(SiCl_3)(H)$ and *cis*-$M(CO)_4(SiCl_3)_2$ (M = Fe, Ru, Os) with PPh_3 indicates the $SiCl_3$ group exhibits a large *trans* effect when bonded to ruthenium. Further substitution in $Ru(CO)_3L(SiCl_3)_2$ is influenced by the nature of L and the incoming ligand.

In 1972 we reported the remarkable stereospecific exchange of *cis*-$Ru(CO)_4(SiCl_3)_2$ with ^{13}CO [1]. Only the CO groups *trans* to the $SiCl_3$ ligands undergo substitution. Further study of this unique compound was hampered by the tedious separation of the *cis* isomer from the *trans* form.

We now find that ultraviolet irradiation of $Ru_3(CO)_{12}$ in hexane with excess Cl_3SiH under 2 atmospheres of carbon monoxide (in a quartz Carius tube) results in almost quantitative formation of *cis*-$Ru(CO)_4(SiCl_3)_2$ after three days.

The method is readily extended to the iron and osmium analogues. The iron compound [2] is known to exist as a mixture of *cis* (80%) and *trans* (20%) forms in equilibrium at room temperature [3]. Heating solutions of *cis*-$Os(CO)_4(SiCl_3)_2$ (m.p. 135—136°C, ν(CO) 2153m, 2095s, 2080vs cm^{-1}, h*) to temperatures above 120°C causes almost complete isomerization to the known [4] *trans* isomer (ν(CO) 2080vs cm^{-1}, h). This may be compared to *cis*-$Ru(CO)_4(SiCl_3)_2$ which isomerizes above 70°C to an equilibrium mixture containing approximately 70% of the *trans* form [5].

As expected *cis*-$Ru(CO)_4(SiCl_3)_2$ (in hexane) readily undergoes substitution with PPh_3 at room temperature. The rate of formation of *mer*-$Ru(CO)_3(PPh_3)(SiCl_3)_2$ (m.p. 204—206°C, ν(CO) 2113w, 2068m, 2047vs cm^{-1}, h) is comparable to the rate of ^{13}CO exchange of the parent molecule. In contrast, the corresponding iron and osmium complexes required temperatures of 100 and 130°C, respectively, to effect substitution by PPh_3.

A similar pattern was observed in the reaction with mesitylene. $[C_6H_3(CH_3)_3]Ru(CO)(SiCl_3)_2$ (ν(CO) 2004 cm^{-1}, c; ^1H NMR δ 6.32 (CH), 2.64 (CH_3) ppm, d) was formed in excellent yield after refluxing *cis*-$Ru(CO)_4(SiCl_3)_2$ in mesitylene

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*Solvent: b = benzene, c = CH_2Cl_2, d = $CDCl_3$, h = hexane. Satisfactory C/H analysis has been obtained for all complexes reported here.

for only 20 minutes. In contrast, $Fe(CO)_4(SiCl_3)_2$ decomposed in refluxing mesitylene over two days and with $Os(CO)_4(SiCl_3)_2$ only a very slow reaction was observed. However, heating $Os(CO)_4(SiCl_3)_2$ at 200°C with mesitylene (in an evacuated sealed tube) did give, in moderate yield, $[C_6H_3(CH_3)_3]Os(CO)(SiCl_3)_2$ (ν(CO) 1997 cm^{-1}, c).

The second equatorial carbonyl ligand in $Ru(CO)_3(PPh_3)(SiCl_3)_2$ does not undergo substitution with PPh_3 even at 80°C. However, it is readily replaced (at room temperature) by $P(OCH_3)_3$ to give $Ru(CO)_2(PPh_3)[P(OCH_3)_3](SiCl_3)_2$ (ν(CO) 2019 cm^{-1}, c). Other factors besides the size of the entering ligand are involved in the substitution of these compounds since the reaction of $Ru(CO)_3[P(OCH_3)_3](SiCl_3)_2$ (ν(CO) 2122, 2082, 2059 cm^{-1}, h) with $P(OCH_3)_3$ to give $Ru(CO)_2[P(OCH_3)_3]_2(SiCl_3)_2$ (ν(CO) 2026 cm^{-1}, c) requires a temperature of 60°C. *Cis* effects are believed important in the substitution of metal carbonyls [6] and further studies of this effect in these compounds are in progress.

If the irradiation of $Ru_3(CO)_{12}$ with Cl_3SiH is stopped after 12 h, it is possible to isolate, by sublimation at 0°C onto a probe cooled to –78°C, *cis*-$Ru(CO)_4(SiCl_3)(H)$ as an air-sensitive, white, crystalline solid melting to a colorless liquid at 22—23°C (ν(CO) 2147w, 2089m. 2074(sh), 2071s cm^{-1}, h; ^{1}H NMR δ –7.35 ppm, b).

The hydride reacts with PPh_3, at a faster rate than *cis*-$Ru(CO)_4(SiCl_3)_2$, to give, in an excellent yield, the moderately air-stable $Ru(CO)_3(PPh_3)(SiCl_3)(H)$ as a white, crystalline solid (m.p. 168°C). This compound does not undergo any reaction with $P(OCH_3)_3$ at ambient conditions. The infrared spectrum (ν(CO) 2105w, 2048m, 2033s cm^{-1}, h) is consistent with a *mer* configuration of the CO groups. The ^{1}H NMR spectrum reveals a high field doublet (δ –6.35 ppm, b) the ^{31}P coupling (14.5 Hz) of which is in agreement with the hydride ligand being *cis* to the PPh_3 [7]. It is concluded that substitution has once again occurred *trans* to the $SiCl_3$ ligand. This indicates that, in this compound, the $SiCl_3$ group has a greater *trans* effect than either carbonyl or hydride ligands, both of which are known to have a large *trans* effect in square planar platinum complexes [8].

Further evidence that there is a labile carbonyl group in this molecule is that the mass spectrum shows as a highest peak ions due to $[P - CO]^+$. Since many homogeneous catalysts have a labile site *cis* to a hydride ligand, the possible catalytic properties of $Ru(CO)_4(SiCl_3)(H)$ are being investigated.

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