Journal of Organometallic Chemistry, 391 (1990) C45–C47
Elsevier Sequoia S.A., Lausanne
JOM 21079PC

Preliminary communication

Preparation and reactivity of $Cp^*Ru(OMe)PCy_3$ and Cp^*RuHL_2 ($L = PCyPh_2$, PCy_2H) from $[Cp^*Ru(OMe)]_2$ and bulky phosphines

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(Received April 9th, 1990)

Abstract

The reaction of $[Cp^*Ru(OMe)]_2$ (**1**) with PCy_3 yields the 16-electron alkoxo derivative, $Cp^*Ru(OMe)(PCy_3)$ (**2**). **2** reacts with H_2 and HBF_4 to give the known $Cp^*RuH_3PCy_3$ (**3**) and $[Cp^*Ru(C_6H_9PCy_2)]BF_4$ (**4**). The reaction of **1** with one or two equivalents of L yields Cp^*RuHL_2 ($L = PCyPh_2$ (**5**), PCy_2H (**6**)) through a β-elimination process. Upon protonation, **5** and **6** are converted into $[Cp^*RuH_2L_2]BF_4$ ($L = PCyPh_2$ (**7**), PCy_2H (**8**)).

As pointed out recently [1], the chemistry of platinum metal alkoxo complexes remains relatively little developed. The chemistry of such ruthenium derivatives was in fact limited to binuclear arene derivatives until the recent preparation by Koelle et al. of $[Cp^*Ru(OMe)]_2$ (**1**) [2]. This compound has a bent structure [1,2] and shows a high reactivity. More specifically, even with weak acids, protonation leads to methanol elimination and formation of a very reactive "Cp^*Ru^+" fragment [3]. It was reported by Wilkinson et al. that methoxo phosphine ruthenium derivatives were unstable towards β-elimination [4], but Koelle et al. have isolated a stable dinuclear dppm methoxo ruthenium compound [2a]. We thought it of interest to determine whether related mononuclear derivatives could exist, and to examine their reactivity.

We describe here the reactions of $[Cp^*Ru(OMe)]_2$ with bulky phosphines; these have resulted in the successful isolation of a 16-electron alkoxo complex containing PCy_3, whereas with slightly less bulky phosphines, β-elimination occurs to give 18-electron hydride complexes, and the products show a very different reactivity towards protonation.

The reaction of $[Cp^*Ru(OMe)]_2$ with PCy_3 in hexane (1 : 2 stoichiometry) does not involve any significant change in the colour of the solution but bright red crystals analyzing for $Cp^*Ru(OMe)(PCy_3)$ (**2**) * can be obtained in 90% yield by

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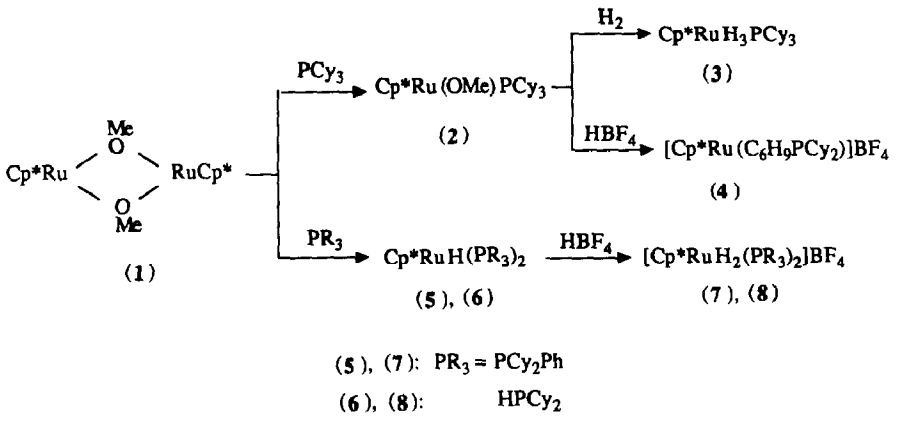

Scheme 1. Reactions of $[Cp^*Ru(OMe)]_2$ with bulky phosphines.

concentration and cooling. Interestingly, this compound was not obtained from the reaction of $Cp^*RuCl(PCy_3)$ with LiOMe [1]. The ^1H NMR spectrum of the complex shows a singlet for the methoxo protons at δ 3.2 ppm (s), (i.e. at higher field than that for **1**), another for the Cp^* ligand at δ 2.0 ppm (s), and a broad multiplet for the phosphine at δ 1–2 ppm. The ^{31}P NMR spectrum shows a singlet at δ 10.0 ppm, and the methoxo carbon signal is observed at δ 70.9 ppm in the $\{^1H\}$ ^{13}C NMR spectrum. The ^{13}C NMR spectrum shows the expected quartet (J(C–H) = 138 Hz).

These data are consistent with the formulation $\{Cp^*Ru(OMe)(PCy_3)\}_n$. However, when the crystal structure of the analogous chloro derivative $Cp^*RuCl(P\text{-}i\text{-}Pr_3)$ [5] is considered, it is difficult to imagine a dinuclear structure for **2**. It is more likely that **2** has a 16-electron monomeric structure.

Complex **2** reacts with H_2 to yield $Cp^*RuH_3(PCy_3)$ (**3**) [5b,6] through heterolytic activation of H_2. This activation is known for complexes containing coordinated amido groups, but not, to the best of our knowledge, for alkoxo derivatives. Protonation of **2** leads to methanol elimination and dehydrogenation of the phosphine ligand to yield $[Cp^*Ru(C_6H_9PCy_2)]BF_4$ (**4**) [7] as in the case of the protonation of **3**.

If **1** is reacted with less bulky phosphines, whatever the stoichiometry, the hydrido bisphosphine derivatives Cp^*RuHL_2 (L = $PCyPh_2$ (**5**), PCy_2H (**6**)) are obtained **. Compounds of this type are known with various ligands [7,8]. **5** and **6** have been characterized by microanalytical and spectroscopic methods. A high field triplet attributed to the hydride is observed near δ −13 ppm (J(PH) ~ 38Hz).

It is clear that in the case of **2** another ligand cannot approach the metal center because of the bulkiness of Cp^* and PCy_3, but it is surprising that a stable 16-electron alkoxo compound can be isolated whereas 18-electron species can not. This is perhaps due to a kinetic stabilization of the methoxo group by the very bulky

* **2**: ^1H NMR in $(CD_3)_2CO$ at 200.132 Hz: δ 3.2 (s), 3H (CH_3O); 2.0 (s), 15 (C_5Me_5); 1.0 (m), 2.5 (m), 33H (C_6H_{11}). ^{13}C NMR in C_6D_6: δ 11.9 ($C_5\mathit{Me}_5$), 27–33 (PCy_3), 70.9 (OMe) and 83 (C_5Me_5).

** **5**: ^1H NMR in $(CD_3)_2CO$ at 200.132 Hz: δ 7.6 (m), 7.2 (m), 20H (Ph); 1.5 (s), 15 H (C_5Me_5), −12.1 (t, J(PH), 35 Hz), 1H (HRu). **6**: ^1H NMR in $(CD_3)_2CO$ at 200.132 Hz: δ 4.8 (AA'XX'), 2H (HP); 2.2 (s), 15H (C_5Me_5); 1–2 (m), 44H (C_6H_{11}) −13.6H (t, J(PH), 38 Hz), 1H (HRu).

PCy_3 ligand. The protons of the CH_3 group may be prevented from approaching the metal centre in this case, but not in that of $PCyPh_2$ and PCy_2H, thus accounting for the β-elimination reaction.

Finally, the reactions of **5** and **6** with HBF_4 yield the stable dihydride derivatives $[Cp^*RuH_2L_2]BF_4$ (L = $PCyPh_2$ (**7**), PCy_3H (**8**) * as in the case of the analogous PPh_3 complexes [7]. No formation of dihydrogen derivatives and no dehydrogenation of a cyclohexyl group could be observed in this case [8].

Acknowledgment. X.D.H. thanks the CNRS, PICS France–Venezuela for support.

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* **7**: ^1H NMR in $(CD_3)_2CO$ at 200.132 Hz: δ 7.6 (m), 7.1 (m), 20H (Ph); 1.5 (s), 15H (C_5Me_5); 0.2 (m), 2.0 (m), 22H (C_6H_{11}); −8.3 (t, J(PH), 27 Hz), 1H (HRu). **8**: ^1H NMR in $(CD_3)_2CO$ at 200.132 Hz: δ 4.9 (AA'XX'), 2H (HP); 2.2 (s), 15H (C_5Me_5); 1–2 (m), 44H (C_6H_{11}); −8.8 (t, J(PH), 28 Hz), 2H (RuH_2).