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Preliminary communication

Effect of ion-pairs on the stereochemistry of decarbonylation of acetyl iodide complexes of ruthenium: evidence of anion catalysis in the CO insertion

Gianfranco Bellachioma, Giuseppe Cardaci, Alceo Macchioni
and Gustavo Reichenbach

Dipartimento di Chimica, Università di Perugia, Via Elce di Sotto, 8, I-06100, Perugia (Italy)

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Abstract

Decarbonylation of *cis,trans*-$[Ru(^{13}CO_a)(CO_b)(PMe_3)_2(COMe)I]$ (2) in the presence of $NaBPh_4$ is stereospecific and gives $[Ru(CO_a)(CO_b)(^{13}CO_b)(PMe_3)_2Me]^+$ (3) (*a* and *b* indicate CO *trans* or *cis*, respectively, to the methyl or the acetyl group); by the principle of microscopic reversibility this demonstrates that the inverse process of insertion is catalyzed by anions.

The effect of ion-pairs on the reaction rates of CO insertion in anionic complexes of iron [1] has been extensively studied and has been attributed to the interaction of cations with the lone pair of the CO [2], which prepares the CO carbon for methyl migration. Information on the effect of ion-pairs in cationic complexes is lacking. In such a case the anion is itself often a nucleophile and it is difficult to distinguish the effect of the ion-pair from that of the nucleophile.

Recently, we observed an anion catalytic effect [3] in isocyanide insertion in cationic iron(II) complexes and, some time ago, Halpern and co-workers observed a similar catalytic effect on the olefin insertion in palladium complexes [4]. This catalytic effect was attributed mainly to the formation of ion-pairs [3]: electrostatic interaction pushes the anion into the coordination sphere of the cations and compels the alkyl to migrate. It is to be expected that this catalytic effect would also be present in the insertion of carbon monoxide: in fact, a positive effect of ion-pair formation was observed in CO insertion in cationic complexes [5] but this might be attributed either to a nucleophilic or to an ion-pair anion effect.

In order to discriminate between these two effects, we studied the decarbonylation reaction of organometallic acetyl halides (Scheme 1), considering that, if an ion-pair catalytic effect were present, the decarbonylation reaction should be stereospecific, since the ionization of halides must be concurrent with the migra-

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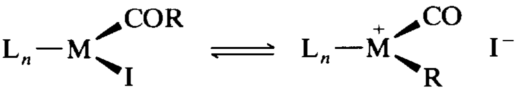
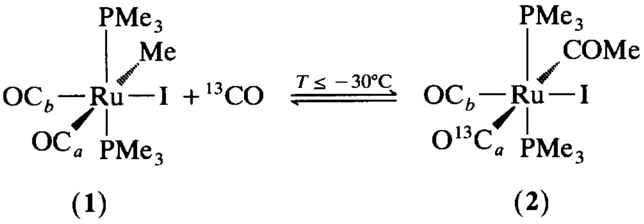
Correspondence to: Dr. G. Cardaci, Dipartimento di Chimica, Università di Perugia, Via Elce di Sotto, 8, I-06100, Perugia, Italy.



Scheme 1

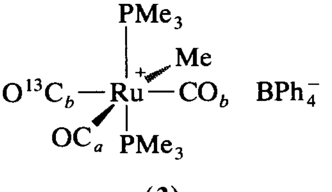


Scheme 2

tion of the alkyl to metal. To study the stereochemistry of the reaction we selected the methyl complex of ruthenium [6] [Ru(CO)$_2$(PMe$_3$)$_2$MeI] (**1**), which gives stereospecific CO insertion according to Scheme 2. The stereoschemistry of *cis,trans*-[Ru(^{13}CO$_a$)(CO$_b$)(PMe$_3$)$_2$(COMe)I] (**2**) was ascertained by ^{1}H and ^{13}C NMR chemical shifts and coupling constants (^{1}H NMR (CD$_2$Cl$_2$): δ(Me) = 2.53 s; ^{13}C NMR (CD$_2$Cl$_2$): δ(CO$_a$) = 193.0 t, ^2J(CO$_a$–P) = 8.5 Hz) [6,7].

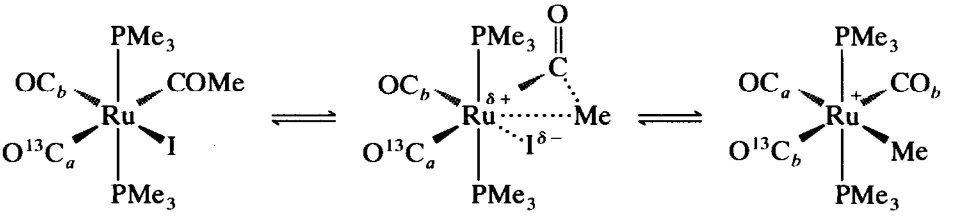
Complex **2** reacts in CH$_3$OH at −30°C with NaBPh$_4$ giving complex **3** (its structure is shown in Fig. 1). Complex **3** was characterized by IR and ^{1}H, ^{31}P, and ^{13}C NMR (IR (CH$_2$Cl$_2$): 2098.0 (w), 2045.5 (s) and 2012.0 (s) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$): δ(Me) = −0.18 td, ^3J(Me–P) = 7.1 Hz, ^3J(Me–CO$_b$) = 1.9 Hz; δ(PMe$_3$) = 1.61 m, $|^2J$(H–P) + ^4J(H–P)$|$ = 7.9 Hz; ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ(P) = −9.57 d, ^2J(P–CO$_b$) = 13.5 Hz; ^{13}C NMR (CD$_2$Cl$_2$): δ(CO$_b$) = 194.2 tq, ^2J(CO$_b$–P) = 13.5 Hz, ^3J(CO$_b$–Me) = 2.0 Hz; δ(CO$_a$) = 187.9 t, ^2J(CO$_a$–P) = 8.8 Hz). The ^{13}C chemical shifts of the CO ligands and the ^{13}C–P and CH_3–^{13}CO coupling constants are consistent with the proposed structure [8].

Furthermore, the assignment of the CO resonances to CO$_a$ and CO$_b$ was verified from the intensity ratio of the two ^{13}C NMR bands (1 : 2) in the corresponding totally labeled complex, which was characterized as described elsewhere [7]. After leaving complex **3** in CD$_2$Cl$_2$ for 1–2 days, the CO ligands were scrambled, giving all the possible forms, as shown by the multiplicity of the ^{31}P{^{1}H} NMR signals (^{31}P{^{1}H} NMR: [Ru(CO)$_3$(PMe$_3$)$_2$Me]$^+$ (s), Ru(CO$_a$)(^{13}CO$_b$)(CO$_b$)(PMe$_3$)Me$^+$ (d, ^2J(P–CO$_b$) = 13.5 Hz), Ru(^{13}CO$_a$)(CO$_b$)$_2$(PMe$_3$)$_2$Me$^+$ (d, ^2J(P–

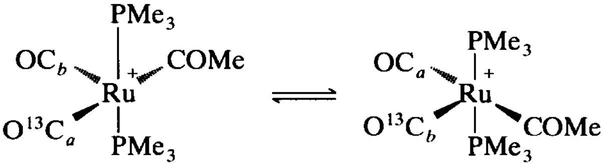


(3)

Fig. 1. Structure of complex **3**.



Scheme 3



Scheme 4

CO_a) = 8.1 Hz), $Ru(CO_a)(^{13}CO_b)_2(PMe_3)_2Me^+$ (t, $^2J(P-CO_b)$ = 13.5 Hz), $Ru(^{13}CO_a)(^{13}CO_b)(CO_b)(PMe_3)_2Me^+$ (dd, $^2J(P-CO_b)$ = 13.5 Hz, $^2J(P-CO_a)$ = 8.1 Hz) and $Ru(^{13}CO)_3(PMe_3)_2Me^+$ (td, $^2J(P-CO_b)$ = 13.5 Hz, $^2J(P-CO_a)$ = 8.1 Hz). This suggests a Ru–CO dissociative process for the scrambling, as has been observed for the corresponding complex of iron [9].

The IR spectrum of complex **3** shows three, rather than two, CO stretching bands in the unlabelled complex [10]; an isotopic shift of 51 cm^{-1} is observed in all the CO stretching bands, indicating that one CO group is substituted by ^{13}CO [11].

The formation of complex **3** during the ionization reaction has interesting mechanistic implications. In fact, this result can be explained either i) *via* a Ru–I bond ionization concerted with the methyl migration according to Scheme 3, or ii) *via* a two-step mechanism with the formation of a pentacoordinate intermediate which isomerizes at a rate slower than that of the methyl migration (Scheme 4). Since theoretical studies [12] and experimental results on the isocyanide insertion reaction in $[Fe(CO)_2L_2(CNR)CH_3]BPh_4$ [6] indicate a fast isomerization of the pentacoordinate intermediate, explanation ii) should probably be excluded.

In agreement with the principle of microscopic reversibility [13], the inverse reaction of iodide with the cationic complex **3** to give the acetyl complex **2** should proceed by the same reaction pathway. Therefore, iodide should catalyze CO insertion, as observed for isocyanide [3] and olefin insertion [4].

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