Journal of Organometallic Chemistry, 390 (1990) C57–C60
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20960PC

Preliminary communication

Reaction of alkenyl carbonyl ruthenium(II) complexes with t-butyl isocyanide. Synthesis of η^1-acylruthenium(II) complexes by intramolecular CO insertion

Julio Montoya, Amelia Santos *
Instituto de Ciencia de Materiales de Madrid, Sede D, CSIC, Serrano 113, 28006 Madrid (Spain)

Antonio M. Echavarren *
Instituto de Química Orgánica, CSIC, Juan de la Cierva 3, 28006 Madrid (Spain)

and Josep Ros
Departament de Química, Universitat Autónoma de Barcelona, 08193-Bellaterra, Barcelona (Spain)

(Received March 9th, 1990)

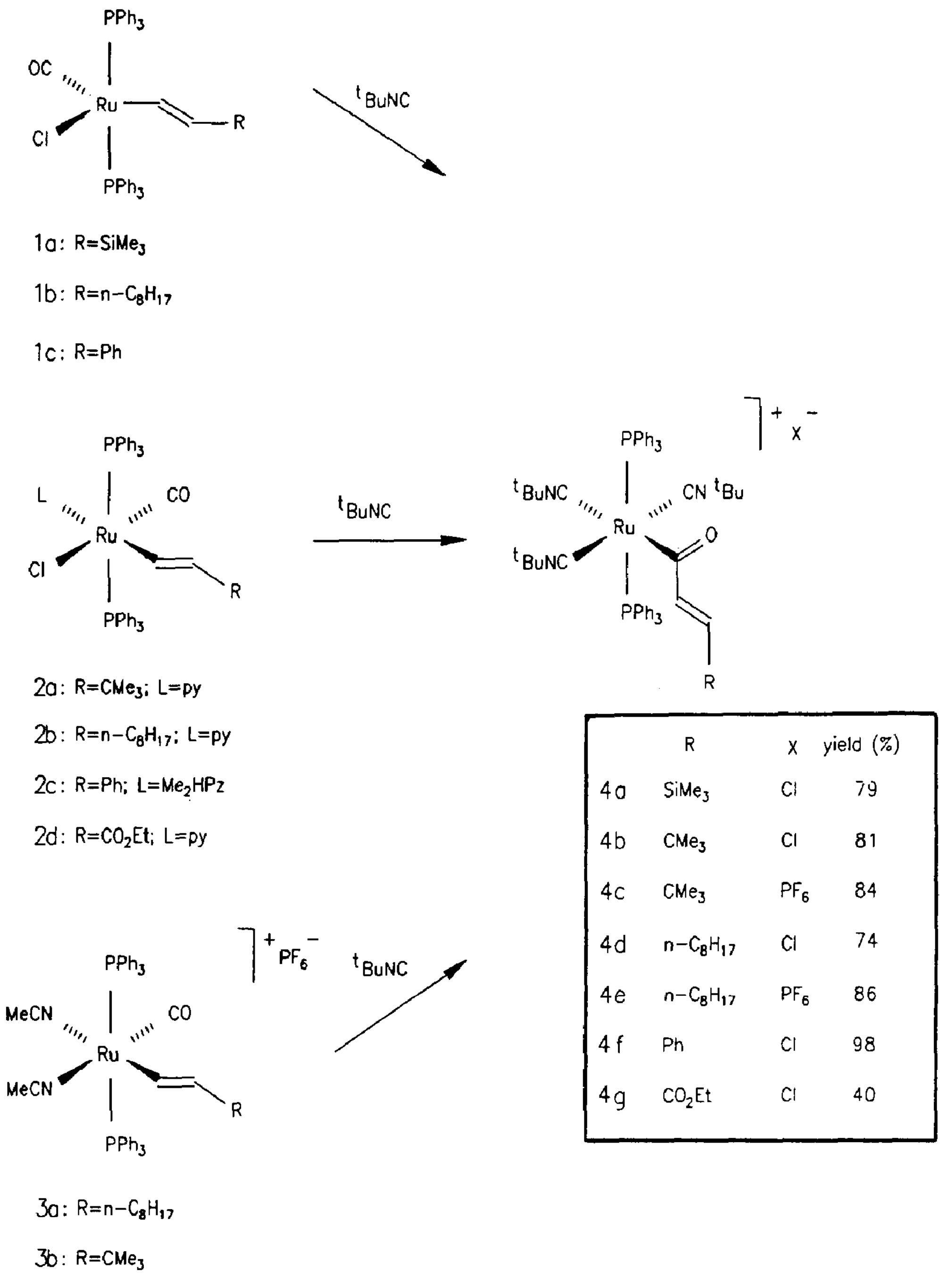
Abstract

Reaction of $Ru(CO)Cl(CH{=}CHR)(PPh_3)_2$ or $Ru(CO)Cl(CH{=}CHR)(PPh_3)_2L$ (L = py, Me_2Hpz) with 1 equivalent of t-butyl isocyanide gives the alkenyl derivatives $Ru(CO)Cl(CH{=}CHR)(PPh_3)_2(t\text{-}BuNC)$. When an excess of isocyanide is used, further reaction results in intramolecular CO insertion to yield η^1-acyl complexes $[Ru(COCH{=}CHR)(t\text{-}BuNC)_3(PPh_3)_2]Cl$. Related complexes were obtained from $[Ru(CO)(CH{=}CHR)(MeCN)_2(PPh_3)_2]PF_6$ and an excess of isocyanide.

Addition of strongly coordinating ligands to transition metal complexes containing both carbonyl and σ-bonded carbon ligands usually results in the formation of acyl complexes by intramolecular CO insertion [1,2]. We report here the successful exploitation of this strategy for the preparation of ruthenium(II) η^1-acyl complexes by reaction of the readily available alkenyl ruthenium(II) complexes with an excess of t-BuNC.

A variety of alkenyl ruthenium(II) complexes can be made by insertion of alkynes into the Ru–H bond of neutral [3–6] or cationic ruthenium hydrides [7]. Some of these alkenyl complexes undergo insertion of a second molecule of the activated alkynes dimethyl acetylenedicarboxylate or propiolic acid esters to give butadienyl ruthenium derivatives in which one of the alkoxycarbonyl groups is coordinated to the metal atom through the carbonyl oxygen [3]. Derivatization can also be accomplished by reaction with CS_2 to give ethenyl dithiocarboxylate complexes [8]. On the other hand, reaction with CO furnishes η^2-acyl complexes [9].

Recently it was reported that the reaction of coordinatively unsaturated ruthenium alkenyl derivatives with methyl or benzyl isocyanide results exclusively in the coordination of the added ligand to the metal to give coordinatively saturated



	R	X	yield (%)
4a	$SiMe_3$	Cl	79
4b	CMe_3	Cl	81
4c	CMe_3	PF_6	84
4d	$n-C_8H_{17}$	Cl	74
4e	$n-C_8H_{17}$	PF_6	86
4f	Ph	Cl	98
4g	CO_2Et	Cl	40

Scheme 1

complexes [10]. However, when a solution of one of the five-coordinated alkenyl derivatives **1a**–**1c** in dichloromethane was stirred with 4 molar equivalents of t-BuNC at 23° C for 10–20 min, a clean conversion into the η^1-acyl complexes **4a** *, **4d**, and **4f**, respectively, was observed (Scheme 1). Related complexes were obtained starting from the coordinatively saturated derivatives **2a**–**2c** or the cationic bisacetonitrile complexes **3a** and **3b**. In all cases the starting complex was rapidly converted into the acyl derivatives **4** within a few minutes, as shown by ^{1}H NMR spectroscopic monitoring of the reaction in deuterochloroform or deuterobenzene at 23–30° C. However, in the case of the ethoxycarbonyl ethenyl derivative **2d** heating in ethanol under reflux for 3–4 h was required to bring about the insertion. This result is in keeping with the known lower activity in the migratory insertion of σ-bonded carbon ligands bearing electron-withdrawing substituents [1].

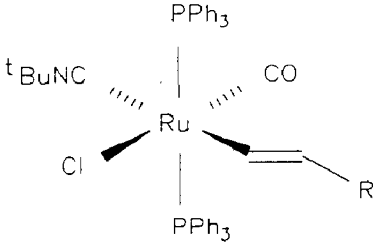
The ^{1}H NMR spectra of the acyl complexes **4** showed two doublets corresponding to the olefinic protons, which are not coupled with the phosphorous atoms, and two singlets in a 1 : 2 ratio between 1.20 and 1.05 ppm, corresponding to the three isocyanide ligands. The ^{13}C NMR spectra showed a characteristic low field triplet at 258.5–257.8 ppm assigned to the η^1-acyl carbonyl coupled to two equivalent phosphorous atoms [11–13]. The ^{13}C NMR coupled spectrum of complex **4b** showed further splitting of this signal because of coupling with the olefinic protons. Two broad resonances were also observed at 149.5–148.2 ppm and 147.5–146.8 ppm, corresponding to the mutually *trans* isocyanides and the *cis* isocyanide, respectively. Other spectroscopic features were consistent with the assigned structures.

When the reaction of complexes **1** or **2** was carried out with 1 molar equivalent of t-BuNC in dichloromethane at 23° C, the corresponding hexacoordinated complexes **5** were isolated in excellent yields (86–92%). Small amounts of the acyl complexes were also detected when the reaction was monitored by ^{1}H NMR spectroscopy in deuterochloroform or deuterobenzene solutions. The stereochemistry shown for **5a**–**5c** was assigned on the basis of their IR, ^{1}H, and ^{13}C NMR spectra and by comparison with data for related six-coordinated ruthenium(II) complexes [3,10]. No other intermediates could be isolated from the reaction of electron releasing substituted alkenyl derivatives. However, with the less reactive ethoxycarbonyl ethenyl ruthenium complex, a second compound **6** was isolated after a mixture of **2d** and t-BuNC in ethanol had been heated under reflux for 30 min. In the ^{1}H NMR spectrum of this complex there were two singlets, at 1.06 and 1.04 ppm, corresponding to mutually *cis* t-BuNC ligands. An analogous complex was also isolated from the reaction of the coordinatively unsaturated complex Ru(CO)Cl(PhC=CHPh)(PPh$_3$)$_2$. Probably, related complexes were also involved in the pathway leading to the η^1-acyl complexes. It is noteworthy that, although in these intermediates both *cis* isocyanide and carbonyl ligands were available for intramolecular migratory insertion [12,14–17], exclusive migration of the alkenyl to the carbonyl ligand was

---

* *Selected spectroscopic data for* ***4a***: IR (KBr, cm^{-1}): 3040 w ν(C–H), 2970 w ν(C–H), 2190 m ν(C≡N), 2130 s ν(C≡N), 1585 m ν(C=O). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.55–7.35 (m, 30 H), 6.05 (d, J = 18.2 Hz, 1H), 5.08 (d, J = 18.2 Hz, 1H), 1.17 (s, 9H), 1.08 (s, 18H), −0.21 (s, 9H). ^{13}C{^{1}H} NMR (CDCl$_3$, 50 MHz): δ 257.8 (t, J = 9.4 Hz, C=O), 153.1 (s, C=C), 148.3 (br, 2 C≡N), 146.8 (br, 1 C≡N), 133.6 (t, J = 4.6 Hz, PPh$_3$), 133.4 (t, J = 5.4 Hz, PPh$_3$), 130.2 (s, PPh$_3$), 127.9 (t, J = 4.6 Hz, PPh$_3$), 126.7 (s, C=C), 57.6 (s, 1 *C*Me$_3$), 57.3 (s, 2 *C*Me$_3$), 29.4 (s, 1 C*Me*$_3$), 29.2 (s, 2 C*Me*$_3$), −1.7 (s, SiMe$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, 32.4 MHz): δ 36.8.

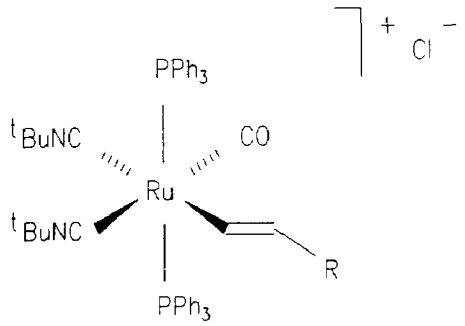
observed. Presumably, the primary insertion product, an unsaturated 16-electron species, is efficiently trapped by the isocyanide to yield the hexacoordinated ruthenium compounds 4.



5a: R=SiMe$_3$

5b: R=Ph

5c: R=CO$_2$Et



6, R=CO$_2$Et

Further studies on the above and related reactions, as well as of their synthetic application, are in progress.

Acknowledgment. We gratefully acknowledge financial support of this work by the Dirección General de Investigación Científica y Técnica (Project PB87-0201-C03-02). We also thank Dr. M.R. Torres for some preliminary studies.

References

1 J.P. Collman, L.S. Hegedus, J.R. Norton and R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987; J.J. Alexander, in: F.R. Hartley, (Ed.), The Chemistry of The Metal–Carbon Bond, Wiley, New York, 1985, Vol. 2.
2 G. Cardaci, G. Reichenbach, G. Bellachioma, B. Wassink and M.C. Baird, Organometallics, 7 (1988) 2475.
3 M.R. Torres, A. Vegas, A. Santos and J. Ros, J. Organomet. Chem., 309 (1986) 169; M.R. Torres, A. Vegas, A. Santos and J. Ros, J. Organomet. Chem., 326 (1987) 413; M.R. Torres, A. Santos, J. Ros and X. Solans, Organometallics, 6 (1987) 1091; A.M. Castaño, A.M. Echavarren, J. López and A. Santos, J. Organomet. Chem., 379 (1989) 171.
4 A. Romero, A. Santos and A. Vegas, Organometallics, 7 (1988) 1988.
5 A. Romero, A. Santos, J. López and A.M. Echavarren, submitted for publication.
6 H. Werner, M.A. Esteruelas and H. Otto, Organometallics, 5 (1986) 2295.
7 J. López, A. Romero, A. Santos, A. Vegas, A.M. Echavarren and P. Noheda, J. Organomet. Chem., 373 (1989) 249.
8 M.R. Torres, A. Perales and J. Ros, Organometallics, 7 (1988) 1223.
9 M.R. Torres, A. Perales, H. Loumhrari and J. Ros, J. Organomet. Chem., 385 (1990) 379.
10 H. Werner, U. Meyer, K. Peters and H.G. Schnering, Chem. Ber. 122 (1989) 2097.
11 C.F.J. Barnard, J.A. Daniels and R.J. Mawby, J. Chem. Soc., Dalton Trans., (1979) 1331.
12 K.M. McCooney, E.J. Probitts and R.J. Mawby, J. Chem. Soc., Dalton Trans., (1987) 1713.
13 D.L. Reger, S.A. Klaeren, J.E. Babin and R.D. Adams, Organometallics, 7 (1988) 181.
14 Y. Yamamoto and H. Yamazaki, Coord. Chem., Rev., 8 (1972) 225.
15 W.R. Roper, G.E. Taylor, J.M. Waters and L.J. Wright, J. Organomet. Chem., 157 (1978) C27.
16 R.D. Adams and D.F. Chodosh, Inorg. Chem., 17 (1978) 41.
17 C.J. Cardin, D.J. Cardin, H.E. Parge and A.C. Sullivan, J. Chem. Soc., Dalton Trans., (1986) 2315.