Vinyl Group Transfer via Insertion: Cluster-Mediated Production of Poly(phenylacetylene), Enynes, and α,β-Unsaturated Aldehydes

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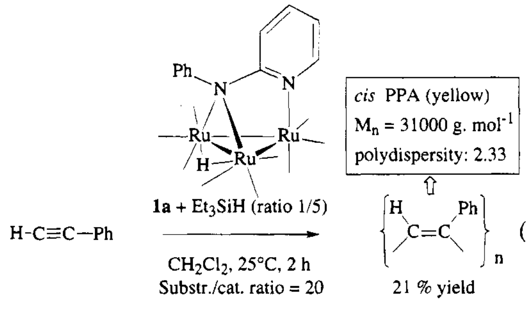
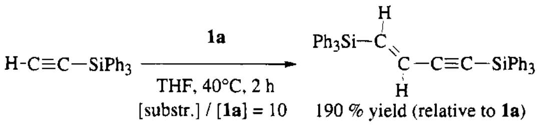
Summary: Whereas polymerization of phenylacetylene takes place at 25 °C under hydrosilylation conditions in the presence of $Ru_3\{\mu\text{-}H\}\{\mu\text{-}RN(C_5H_4N)\}(CO)_9$ *(**1a**, R =* C_6H_5*; **1b**, R =* CH_3*), selective dimerization of (triphenylsilyl)acetylene to (E)-1,4-bis(triphenylsilyl)-but-1-en-3-yne is observed in the absence of silane. Attempts to mimic the addition of a second ligand to the vinyl intermediate **2** were made: (i) benzyl isocyanide undergoes insertion into the metal–vinyl bond of **2a** to give **3a**, bearing a coordinated vinylimino ligand; (ii) parallel migratory CO insertion is induced either by addition of phosphines to **2b**, to give the disubstituted propenoyl derivative **4b**, or by addition of CO to yield the trappable propenoyl adduct **5b**, which reacts further with hydrogen to produce α-phenylcinnamaldehyde.*

Recent discoveries of metal-promoted polymerization of phenylacetylene under hydrosilylation conditions[1] prompt us to report observations in the chemistry of the cluster complex $Ru_3\{\mu\text{-H}\}\{\mu\text{-RN}(C_5H_4N)\}(CO)_9$ (**1a**, R = C_6H_5; **1b**, R = CH_3). Complex **1a** was earlier shown to promote the stoichiometric hydrovinylation of diphenylacetylene via transient formation of the alkenyl species $Ru_3\{\mu\text{-PhC=CHPh}\}\{\mu\text{-PhN}(C_5H_4N)\}(CO)_8$ (**2a**).[2] In attempting to examine the potential activity of **1** in the hydrosilylation of phenylacetylene, we noted the formation of an abundant yellow precipitate at room temperature, subsequently identified as a stereoregular *cis*-poly(phenylacetylene).[3] It was subsequently found that the polymerization can be initiated either from **1** or **2** and requires only small amounts of triethylsilane ([Et_3SiH] /[**1a**] ≅ 5) (eq 1).[4]



(1)

Polymer formation is rapid within the first minutes but decreases after a few hours with the disappearance of the principal observable species, namely the vinyl complex **2**.[5] When the reaction is performed in the absence of silane, crystals of 1,2,4-triphenylbenzene are obtained.[6,7] On the other hand, when (triphenylsilyl)acetylene is treated with **1a** (in the absence of Et_3SiH), glittering crystals of (*E*)-1,4-bis(triphenylsilyl)-but-1-en-3-yne are progressively formed on the walls of the glass vessel (eq 2). They are separated by filtration and isolated in 190% yield.[8,9]



$$\text{H-C}\equiv\text{C-SiPh}_3 \xrightarrow[\text{THF, 40°C, 2 h}]{\textbf{1a}} \text{Ph}_3\text{Si-}\overset{\text{H}}{\text{C}}\text{=}\underset{\text{H}}{\text{C}}\text{-C}\equiv\text{C-SiPh}_3 \qquad (2)$$

[substr.] / [**1a**] = 10   190 % yield (relative to **1a**)

No isolable intermediates[9,10] other than the vinyl species **2** are seen in this selective dimerization. We thus looked for susceptible substrates to mimic the addition of a second molecule of (triphenylsilyl)acetylene and to show us what was the more accessible coordination site onto the vinyl complex. Introducing benzyl isocyanide for this purpose, we observed its facile incorporation (eq 3) to give the new complex $Ru_3\{\mu\text{-PhCH}_2\text{N=CC(Ph)=CHPh}\}\{\mu\text{-PhN}(C_5H_4N)\}(CO)_8$ (**3a**,

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(1) (a) Goldberg, Y.; Alper, H. *J. Chem. Soc., Chem. Commun.* **1994**, 1209. (b) Yamamoto, H.; Mondoh, K.; Fuchikami, T. *Tetrahedron Lett.* **1994**, *35*, 4137.

(2) (a) Lugan, N.; Laurent, F.; Lavigne, G.; Newcomb, T. P.; Liimatta, E.; Bonnet, J.-J. *J. Am. Chem. Soc.* **1990**, *112*, 8607. (b) Lugan, N.; Laurent, F.; Lavigne, G.; Bonnet, J.-J. *Organometallics* **1992**, *11*, 1351.

(3) For synthetic routes to polyphenylacetylene, see: (a) Masuda, T.; Higashimura, T. *Acc. Chem. Res.* **1984**, *17*, 51 and references therein. (b) Navarro, F. R.; Farona, M. F. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2335. (c) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422. (d) Sen, A.; Lai, T.-W. *Organometallics* **1982**, *1*, 415. (e) Katz, T. J.; Ho, T. H.; Shih, N.-Y., Ying, Y.-C.; Stuart, V. I. W. *J. Am. Chem. Soc.* **1984**, *106*, 2659. (f) Furlani, A.; Napoletano, C.; Russo, M. V.; Camus, A.; Marsich, N. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 75. (g) Yamaguchi, I.; Osakada, K.; Yamamoto, T. *Inorg. Chim. Acta* **1994**, *220*, 35. (h) Haupt, H.-J.; Ortmann, U. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1209. (i) Amer, I.; Schumann, H.; Ravindar, V.; Baidossi, W.; Goren, N.; Blum, J. *J. Mol. Catal.* **1993**, *85*, 163.

(4) (a) Preparation of the polymer: PhC≡CH (0.757 mL, 7 mmol); Et_3SiH (0.275 mL, 1.71 mmol); **1a** (250 mg, 0.345 mmol); CH_2Cl_2, 20 mL; t = 25 °C. A yellow precipitate appears after a few minutes. After 2 h, acetone is added to ensure complete precipitation. The solid residue is washed with acetone and dried under vacuum (150 mg, 21% yield). GPC analysis (THF) gives M_n = 31 200 and polydispersity 2.33. Small amounts of $(HC\equiv CPh)_3$ are also detected. (b) *cis*-PPA: ^{1}H NMR ($CDCl_3$) δ 7.0 (m, 3H), 6.7 (m, 2H), 5.82 (s, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 143.6 (C quat), 140.0 (C ipso, Ph), 132.5 (C methyne), 128 (Ph); mp 216.7–218.2 °C.

(5) (a) Oxidative addition of $HSiR_3$ to aminopyridine derivatives of type **1** takes place only at $t > 85$ °C.[5b,c] The silane derivative $Ru_3\{\mu\text{-H}\}_2\{\mu\text{-PhN}(C_5H_4N)\}(SiEt_3)(CO)_8$ may be used as an alternate catalyst precursor in the absence of free silane; it is rapidly converted into **2** during the polymerization at 25 °C. (b) Cabeza, J. A.; Llamazares, A.; Riera, V.; Triki, S.; Ouahab, L. *Organometallics* **1992**, *11*, 3334. (c) Cabeza, J. A.; Garcia-Granda, S.; Llamazares, A.; Riera, V.; Van der Maelen, J. F. *Organometallics* **1993**, *12*, 2973.

(6) 1,2,4-Triphenylbenzene[7d] was identified by MS (EI, *m/z* 306 (M^+)), isolated in 17% yield, and characterized by a rapid X-ray analysis. Crystal data: orthorhombic, *Pbca*, a = 10.426(1) Å, b = 17.887(5) Å, c = 18.474(2) Å, Z = 8.

(7) For leading references on metal-mediated alkyne oligomerization, see: (a) Schore, N. *Chem. Rev.* **1988**, *88*, 1081. (b) Adams, R. D.; Babin, J. E.; Tasi, M.; Wang, J.-G. *Organometallics* **1988**, *7*, 755. (c) Knox, S. A. R. *J. Cluster Sci.* **1992**, *3*, 385. (d) Mantovani, A.; Marcomini, A.; Belluco, U. *J. Mol. Catal.* **1985**, *30*, 73. (e) Süss-Fink, G.; Meister, G. *Adv. Organomet. Chem.* **1993**, *35*, 41–134.

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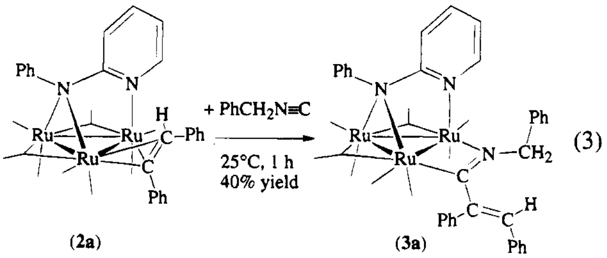
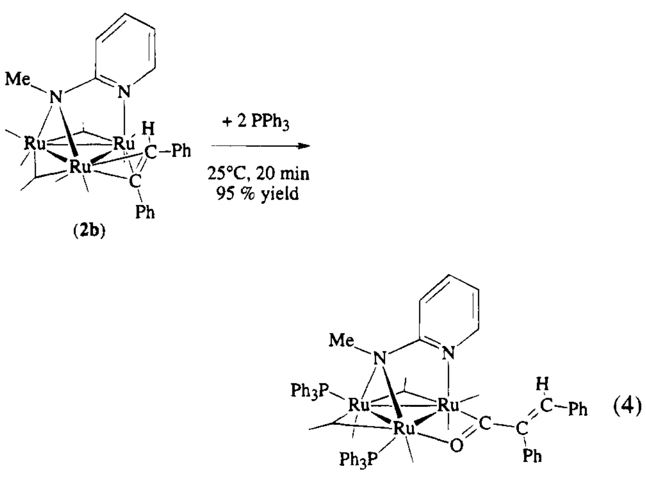
40% yield) bearing an edge-bridging vinylimino ligand, as revealed by an X-ray analysis.[11]



(2a) (3a) (3)

This rapid insertion reaction suggested that migratory CO insertion might also be feasible. Effectively, when **2b** is treated with triphenylphosphine, rapid uptake of *two* PPh_3 molecules is observed, leading to the propenoyl derivative $Ru_3\{\mu\text{-}O{=}C(C(Ph){=}CHPh)\}\{\mu\text{-}CH_3N(C_5H_4N)\}(CO)_6(PPh_3)_2$ (**4b**; 95% yield) (eq 4).[12]



(2b) (4b) (4)

We suggest that the addition of the first phosphine causes migratory CO insertion, whereas facile capture of the second ligand is brought about by the additional CO labilization induced by the newly formed propenoyl group.[13] These reactions show that *a vinyl group may be transferred away from the metal center while the cluster complex retains the ability to accommodate other incoming substrates in its coordination sphere*. Indeed, vinyl compounds of type **2** were also found to add CO reversibly (1 atm, 25 °C, 5 min). With **2b**, we succeeded in crystallizing the adduct from a CO-saturated solution at 25 °C. Mass spectrometry indicated that uptake of *two carbonyls* had taken place, and the formulation of the compound as the 2,3-diphenylpropenoyl derivative $Ru_3\{\mu\text{-}O{=}CC(Ph){=}CHPh\}\{\mu\text{-}CH_3N(C_5H_4N)\}(CO)_9$ (**5b**) (50e cluster) was established by NMR spectroscopy and X-ray diffraction (Figure 1; see also Scheme 1).[14,15] In contrast to the case of **4b**, the propenoyl group here spans the same metal–metal edge as the amido group, which indicates that a σ–π motion of the vinyl group on the metal–metal edge has taken place at an intermediate stage.

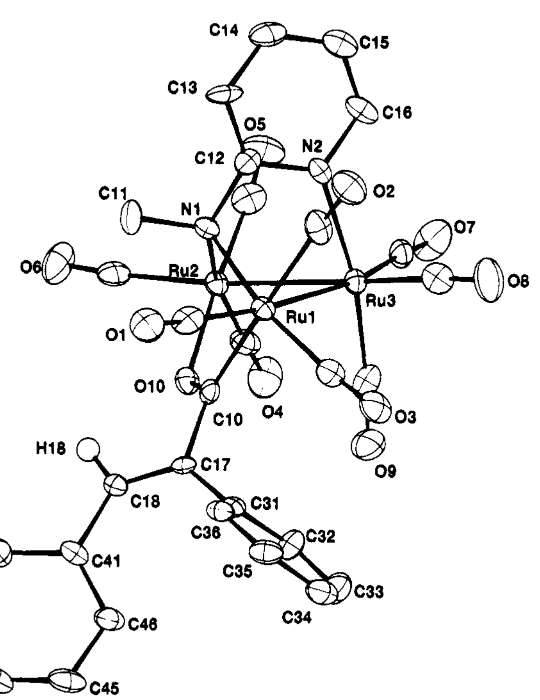


Figure 1. Perspective view of the propenoyl complex **5b**. Selected interatomic distances (Å) and bond angles (deg): Ru(1)··Ru(2), 3.4124(8); Ru(1)–Ru(3), 2.7943(9); Ru(2)–Ru(3), 2.7552(8); Ru(1)–C(10), 2.074(6); Ru(2)–O(10), 2.104(4); C(10)–O(10), 1.245(7); C(10)–C(17), 1.512(7); C(17)–C(18), 1.330(8); Ru(1)–Ru(3)–Ru(2), 75.89(2); Ru(1)–C(10)–O(10), 121.9(4); Ru(2)–O(10)–C(10), 120.3(3).

Though migration of vinyl groups to CO must occur in important catalytic reactions such as the silacarbo-

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(8) (*E*)-1,4-Bis(triphenylsilyl)but-1-en-3-yne: ^1H NMR (CD_2Cl_2) δ 6.66 (AB pattern, 2H, *J*(H–H) = 19.2 Hz); MS (EI) *m/z* 567 (M^+); IR (CH_2Cl_2) $\nu_{C\equiv C}$ 2156 cm^{-1}.

(9) For leading references on metal-mediated syntheses of enynes, see: (a) Trost, B. M.; Chan, C.; Ruhter, G. *J. Am. Chem. Soc.* **1987**, *109*, 3486. (b) Ohshita, J.; Furumori, K.; Matsuguchi, A.; Ishikawa, M. *J. Org. Chem.* **1990**, *55*, 3277. (c) Kovalev, I. P.; Yevdakov, K. V.; Strelenko, Y. A.; Vinogradov, M. G.; Nikishin, G. I. *J. Organomet. Chem.* **1990**, *386*, 139. (d) Bianchini, C.; Peruzzini, M.; Zanobini, F.; Frediani, P.; Albinati, A. *J. Am. Chem. Soc.* **1991**, *113*, 5453. (e) Echavarren, A. M.; Lopez, J.; Santos, A.; Montoya, J. *J. Organomet. Chem.* **1991**, *414*, 393. (f) Dahlenburg, L.; Frosin, K. M.; Kerstan, S.; Werner, D. *J. Organomet. Chem.* **1991**, *407*, 115. (g) Schäfer, M.; Mahr, N.; Wolf, J.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1315. (h) Esteruelas, M. A.; Oro, L. A.; Ruiz, N. *Organometallics* **1994**, *13*, 1507. (i) Barbaro, P.; Bianchini, C.; Peruzzini, M.; Polo, A.; Frediani, P. *Inorg. Chim. Acta* **1994**, *220*, 5.

(10) For isolated intermediates in mononuclear complexes, see also: (a) Albertin, G.; Amendola, P.; Antoniutti, S.; Ianelli, S.; Pelizzi, G.; Bordignon, E. *Organometallics* **1991**, *10*, 2876. (b) Jia, G.; Meek, D. W. *Organometallics* **1991**, *10*, 1444. (c) McMullen, A. K.; Selegue, J. P.; Wang, J.-G. *Organometallics* **1991**, *10*, 3421. (d) Selnau, H. E.; Merola, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 4008.

(11) (a) Preparation of **3a**: solvent CH_2Cl_2 (30 mL); **2a** (350 mg, 0.40 mmol); $PhCH_2NC$ (60 μL, 0.49 mmol); stirred 1 h at 20 °C; chromatography (silica gel, elution with hexane/dichloromethane 4/1). The principal orange band was identified as **3a** (40% yield). IR (CH_2Cl_2): ν_{CO} 2082 w, 2050 s, 2013 vs, 1980 m, 1955 sh, 1890 w, 1810 m, br cm^{-1}. (b) Crystal data for **3a**: monoclinic, $P2_1/c$, a = 17.205(2) Å, b = 11.381(2) Å, c = 19.853(2) Å, β = 90.83(1)°, Z = 4; R = 0.038, R_w = 0.052 for 4968 observations and 328 variable parameters.

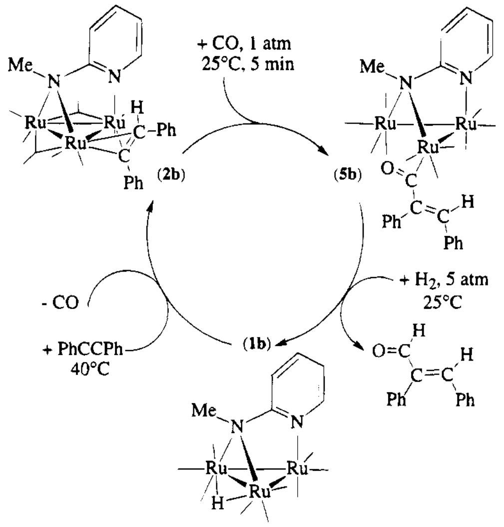
(12) (a) Preparation of **4b**: solvent CH_2Cl_2 (10 mL); **2b** (150 mg, 0.184 mmol); PPh_3 (100 mg, 0.38 mmol); stirred 20 min at 20 °C; red-violet compound **4b** recrystallized from toluene/pentane, 95% yield. (b) Spectroscopic data for **4b**: IR (CH_2Cl_2) ν_{CO} 2007 vs, 1945 br, 1850 mw, 1850 m, br cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 44.1 (d, 1P, J_{PP} = 25.8 Hz), 26.0 (d, 1P). (b) Crystal data for **4b**: monoclinic, $P2_1/n$, a = 14.579(7) Å, b = 16.763(6) Å, c = 27.174(7) Å, β = 100.9(7)°, Z = 4.

(13) (a) Szostak, R.; Strouse, C. E.; Kaesz, H. D. *J. Organomet. Chem.* **1980**, *191*, 243. (b) Mayr, A.; Lin, Y. C.; Boag, N. M.; Kampe, C. E.; Knobler, C. B.; Kaesz, H. D. *Inorg. Chem.* **1984**, *23*, 4640. (c) Kampe, C. E.; Kaesz, H. D. *Inorg. Chem.* **1984**, *23*, 4646. (d) Chen, Y. J.; Knobler, C. B.; Kaesz, H. D. *Polyhedron* **1988**, *7*, 1891.

(14) Spectroscopic data for **5b**: IR (CH_2Cl_2) ν_{CO} 2070 vw, 2047 vs, 2017 s, 1992 vw, 1978 m, 1955 sh cm^{-1}; $^{13}C\{^1H\}$ NMR δ 302 (acyl carbon).

(15) Crystal data for **5b**: monoclinic, $P2_1/c$, a = 10.5997(8) Å, b = 10.002(1) Å, c = 29.720(5) Å, β = 99.13(1)°, Z = 4; R = 0.075, R_w = 0.086 for 4616 observations and 406 variables. (b) Details are provided in the supplementary material.

Scheme 1



nylation of alkynes,[16] propenoyl intermediates are still rarely intercepted in cluster compounds,[17] whereas there are examples of acyl derivatives resulting from alkyl[18] or aryl migration.[19]

Treatment of complex **5b** with hydrogen (25 °C, 5 atm, 3 h) causes elimination of α-phenylcinnamaldehyde and recovery of the hydrido derivative **1b**. The propenal is separated by chromatography and isolated as colorless crystals.[20] The overall transformation, shown in Scheme 1, represents a stepwise stoichiometric hydroformylation of diphenylacetylene and parallels the proposed cycle for olefin hydroformylation catalyzed by $[Ru_3(\mu\text{-}H)(CO)_{11}]^-$.[21]

Catalytic production of α-phenylcinnamaldehyde (778% yield, corresponding to about 8 cycles) was also found to take place under nonoptimized conditions, using **2b** as a catalyst precursor.[22] However, at the end of the catalytic experiment, none of the above species remained in solution, and evidence was obtained that deactivation of the system had taken place via CO insertion into the metal–amido bond.[23] Thus, the viability of the system appears to be presently limited to very mild and specific conditions. Attempts to optimize the lifetime of the catalytic system and to examine its possible extension to a variety of more reactive 1-alkynes are underway.

Even though clusters are not at the point to compete with mononuclear complexes as synthetic tools for organic synthesis, the present contribution shows that they may be of some utility on a laboratory scale for a number of stoichiometric carbon–carbon bond-forming reactions leading to the production of gram quantities of valuable organic products. Suitable combinations of "hemilabile" ligands and stabilizing groups are still to be found in order to solve recurrent problems inherent to their limited lifetime under catalytic conditions.

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Supplementary Material Available: Text giving details of the X-ray structure analysis and tables of crystallographic data, atomic coordinates, anisotropic thermal parameters, and selected interatomic distances and bond angles for **5b** and a table of combustion analysis data for all new compounds (8 pages). Ordering information is given on any current masthead page.

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[16] Ojima, I.; Donovan, R. J.; Ingallina, P.; Clos, N.; Shay, W. R.; Eguchi, M.; Zeng, Q.; Korda, A. *J. Cluster Sci.* **1992**, *3*, 423 and references therein.

[17] Boag, N. M.; Kampe, C. E.; Knobler, C. E.; Kaesz, H. D. *J. Organomet. Chem.* **1988**, *355*, 385.

[18] (a) Kampe, C. E.; Boag, N. M.; Kaesz, H. D. *J. Am. Chem. Soc.* **1983**, *105*, 2896. (b) Lourdichi, M.; Pince, R.; Dahan, F.; Mathieu, R. *Organometallics* **1983**, *2*, 1417.

[19] (a) Blickensderfer, J. R.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 2686. (b) Lugan, N.; Lavigne, G.; Bonnet, J.-J. *Inorg. Chem.* **1987**, *26*, 585.

[20] α-Phenylcinnamaldehyde: IR (CH_2Cl_2) ν_{CO} 1685 cm^{-1}; MS (EI) *m/z* 208 (M^+); ^1H NMR (CD_2Cl_2) δ 9.77 (s, 1H, –C(O)*H*) (vinylic H obscured by phenyl resonances); $^{13}C\{^1H\}$ NMR δ 193.8 (H–*C*=O), 150.1 (C_α), 141.6 (ipso α-Ph), 133.8 (ipso β-Ph), C_β obscured by phenyl resonances.

[21] (a) Suss-Fink, G.; Herrman, G. *J. Chem. Soc., Chem. Commun.* **1985**, 735. (b) Suss-Fink, G.; Schmidt, G. F. *J. Mol. Catal.* **1987**, *42*, 361. (c) Knifton, J. *J. Mol. Catal.* **1987**, *43*, 65. (d) Knifton, J. *J. Mol. Catal.* **1988**, *47*, 99.

[22] (a) Catalytic experiment: solvent CH_2Cl_2 (15 mL); **1b** (70 mg, 0.105 mmol); PhC≡CPh (940 mg, 5.27 mmol); $P(H_2)$ = 15 atm; *P*(CO) = 5 atm; *t* = 70 °C; time 65 h. Chromatographic workup (aluminum oxide) allows separation of the aldehyde as the second band (following unreacted PhC≡CPh). The α-phenylcinnamaldehyde is recrystallized from dichloromethane/hexane (170 mg, 0.817 mmol); 778% yield. Such a compound has not been prepared since 1933.[22b] (b) Shoriguin, P.; Issaguljanz, W.; Matschinskaja, J. *Ber. Dtsch. Chem. Ges. A* **1933**, *66*, 389.

[23] The inactive mixture recovered from the reactor contained crystals of a new dimeric complex characterized as $[Ru\{-C(O)N(CH_3)(C_5H_4N)\}(CO)_3]_2$, shown by an X-ray study to involve the chelating carbamoyl group $-C(O)N(CH_3)(C_5H_4N)$, bound to the metal through the carbonyl ligand and the pyridyl group (details to be published in full later).