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Phenylacetylene dimerization promoted by ruthenium(II) complexes

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Abstract

The complex $Ru(CO)(CH{=}CHPh)Cl(C_5H_5N)(PPh_3)_2$ and related alkenyl complexes react in methanol or ethanol to give (*E*,*E*)-1,4-diphenylbuta-1,3-diene and the ruthenium(II) hydride $Ru(CO)H(Cl)(C_5H_5N)(PPh_3)_3$. Further reaction of this hydride with the butadiene results in 1,2-reduction to yield (*E*)-1,4-diphenyl-1-butene. However, the reaction of phenylacetylene with catalytic amounts of ruthenium hydrides gave the dimer (*Z*)-1,4-diphenylbuten-3-yne. On the other hand, the reaction of 1,2-diphenylethenylruthenium(II) derivatives in methanol or ethanol gave *trans*-stilbene rather than the butadiene. Several deuteriation experiments were performed in order to elucidate the mechanism of formation of (*E*,*E*)-1,4-diphenylbuta-1,3-diene and ruthenium hydride from the corresponding alkenyl complexes.

Introduction

Dimerization, cyclotrimerization, oligomerization, and polymerization of alkynes are important processes in organometallic chemistry [1,2]. As part of a broader study of the reactions of ruthenium hydride complexes with alkynes we have recently observed the formation of small amounts of cyclotrimers in the reaction of $Ru(CO)H(Cl)(PPh_3)_3$ (**1**) [3] with methyl propynoate [4]. We report below the formation of 1,4-diphenylbutadiene and the ruthenium(II) hydrides from phenylethenylruthenium(II) complexes, and some related reactions.

Results and discussion

Refluxing an ethanol solution of complex **2**, the product of insertion of phenylacetylene into the Ru–H bond of hydride $Ru(CO)H(Cl)(C_5H_5N)(PPh_3)_2$ (**3**) [5], gave rise to a mixture of (*E*,*E*)-1,4-diphenylbuta-1,3-diene (**4**) (91%) and the starting hydride **3** (85%). Similar results were obtained when a solution of the

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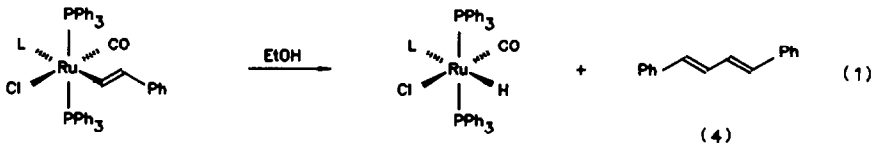
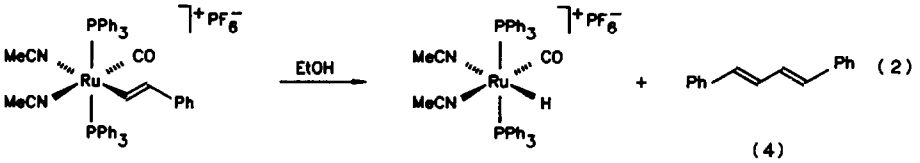


(2, L = py
5, L = 3,5-Me_2Hpz)

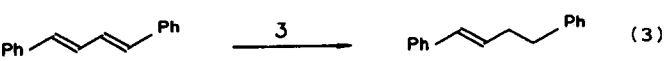
(3, L = py
6, L = 3,5-Me_2Hpz)



(7) (8)

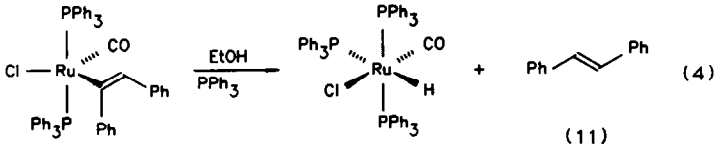
3,5-dimethylpyrazole complex **5** [6] was refluxed for 3 h, yielding **4** (78%) and the corresponding hydride **6** [7] in 81% yield (eq. 1). Likewise refluxing of an ethanol solution of the cationic alkenyl complex **7** for 2 h gave a mixture of hydride **8** [8] (62%) and diene **4** (94%) (eq. 2). This new reaction, when coupled with the insertion of the alkyne into the Ru–H bond [5][8], provides a two-step synthesis of butadiene **4** starting from phenylacetylene and the hydrides **3**, **6** or **8**.

When the ethanolic solution of the alkenyl complex **2** was heated for longer times, the alkene (*E*)-1,4-diphenyl-1-butene (**9**) was isolated as the major product in 65% yield, along with the corresponding hydride **3**. This 1,2-reduction was also brought about by heating butadiene **4** with hydride **3** in ethanol, to give **9** as the only isolated organic product (eq. 3).

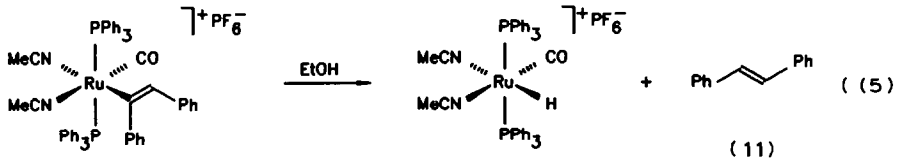


(4) (9)

In contrast to the above results, when the alkenyl complex **10** [9] was heated in ethanol for 20 h in the presence of triphenylphosphine (1 equivalent) the products were *trans*-stilbene (**11**) (83%) and hydride **1** (isolated in 38% yield) (eq. 4). Presumably, ethanolysis of the alkenyl complex, for which an *E*-stereochemistry has been established by X-ray diffraction [9], gave *cis*-stilbene as the initial product, which rapidly isomerizes to **11** through an insertion–elimination process catalyzed by the ruthenium hydride. Similarly, refluxing of a suspension of **12** [8] in ethanol for 4.5 h gave the hydride **8** (73%) and the alkene **11** (71%) (eq. 5). When the reaction was allowed to proceed for only 1–2 h, a small amount of *cis*-stilbene, the initial product of the ethanolysis reaction, was also observed in the reaction solution.

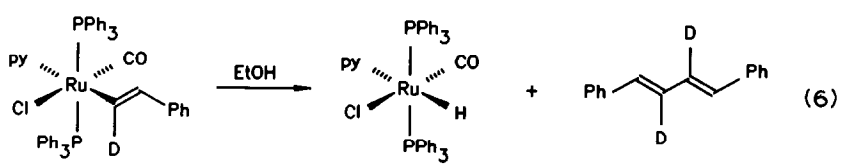


(10) (1) (11) (4)



(12) (8) (11) (5)

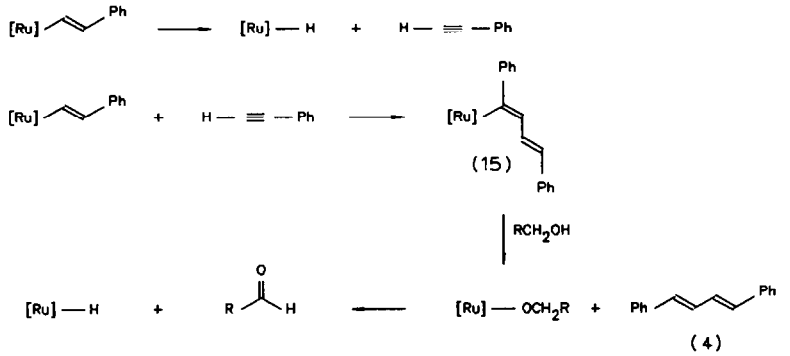
A series of experiments was carried out in order to ascertain the mechanism of the above reactions. When the alkenylruthenium complex **2** was heated in methanol-d_4 at 85°C in a sealed tube, a mixture of hydride **3** and partially deuterated butadiene **4** (ca 50–60% d_2 by ^{1}H NMR) was obtained. The mass spectrum showed that this butadiene was a mixture of d_0–d_4 derivatives. The IR and ^{1}H NMR spectra of the reaction mixtures showed no evidence of the presence of any ruthenium deuteride. In a separate experiment was shown that hydride **2** did not undergo exhange with deuterium under the reaction conditions. These results indicate that the ruthenium deuteride undergoes extensive exchange with deuterated **4** by an insertion–elimination process, leading to the selective formation of C–D bonds, which are stronger than the Ru–D bonds [10]. On the other hand, refluxing of an ethanol solution of the alkenyl ruthenium complex **13**, prepared from deuteriophenylacetylene [11] and **3**, gave the hydride **3** (80%) and (*E*,*E*)-1,4-diphenylbuta-1,3-diene-2,3-d_2 (**14**) (eq. 6).



(13) (3) (14) (6)

Oxidation of 3,4-dimethoxybenzyl alcohol (2.7 equivalent) was shown to take place when it was treated with complex **7** in 1,2-dichloroethane, 3,4-dimethoxybenzaldehyde being formed along with hydride **8**. A related dehydrogenation of primary alcohols to afford aldehydes was previously reported to take place in the reaction of $Ru(O_2CCF_3)_2(CO)(PPh_3)_2$ with diphenylacetylene, trifluoroacetic acid, and a primary alcohol [12].

Finally, when a solution of **12** in methanol-d_4 was kept at 80°C in a sealed tube for 3 h the expected deuterated *trans*-stilbene and deuteride **8**-*d* were formed. The ruthenium deuteride **8**-*d* gave a broad signal at δ −12.90 in the ^{2}H NMR spectrum.



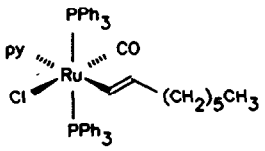
Scheme 1

Analysis of the ^{1}H NMR and mass spectra demonstrated that the stilbene formed in this experiment was a mixture of d_1 and d_2 alkenes (ca 45 : 55 ratio), as expected for insertion of the alkene into the Ru–D bond followed by elimination. Longer reaction times resulted in almost complete deuteriation of the double bond of stilbene, with concomitant build-up of hydride **8**.

The above results suggest that the reaction of the phenylethenyl ruthenium(II) complexes involves an initial β-hydride elimination reaction to give the corresponding hydride and the phenylacetylene, and the latter is then inserted into the ruthenium–carbon bond of the starting alkenyl complex to give a new butadienyl derivative **15** (Scheme 1). Cleavage of the ruthenium–carbon bond by the alcohol would lead to the observed butadiene **4** and a ruthenium(II) alkoxide, which would afford the corresponding hydride and the aldehyde by a further β-hydride elimination reaction. This scheme is consistent with the deuteration experiments and with the oxidation of 3,5-dimethoxybenzyl alcohol to the aldehyde. Formation of **9** by reaction of diene **4** with the ruthenium hydride may proceed by an analogous mechanism involving insertion followed by cleavage of the alkylruthenium derivative by the alcohol.

Hydride **3** was also obtained in 76% yield from the reaction of the 1-octenylruthenium complex **16** [5], while alkenyl complexes **17** and **18** [6] gave hydride **6** in good yields. In these reactions the corresponding dienes were isolated as mixtures of isomers and were not fully characterized. However, under the same conditions, the 2-ethoxycarbonylethenyl and 3,3-dimethyl-1-propenylruthenium complexes **19** and **20** [5] were recovered unchanged.

We recently showed that the reaction of certain cationic ruthenium(II) hydrides, such as **21a** and **21b** [13], with 1-alkynes gives rise to σ-alkynylruthenium(II) complexes [14]. As an exension of this work on the formation of dimers mediated by ruthenium(II) complexes, we decided to examine the reaction of phenylacetylene with cationic hydrides under catalytic conditions. When a toluene solution of phenylacetylene was heated for 24 h with cationic hydride **21a** or **21b** (1–2%) the product was the dimer (*Z*)-1,4-diphenylbuten-3-yne (**22**) [15,16] in 21% yield (eq. 7). After longer reaction times in toluene or the neat alkyne there was some isomerization of the dimer to the *E*-isomer. Similarly, $[Ru(CO)H(CN^tBu)(C_5H_5N)(PPh_3)_2]PF_6$ (**23**), prepared by treating hydride **21b** with 1 equivalent of tert-butyl isocyanide,



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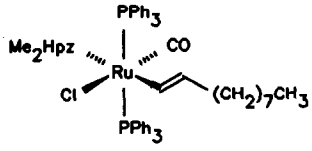

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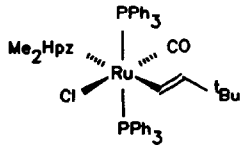

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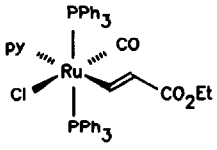

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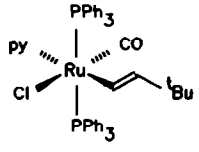
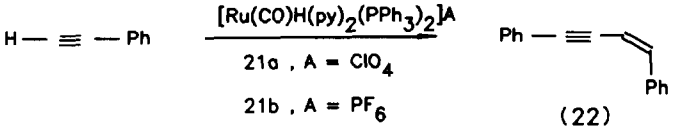


(20)

catalyzed this dimerization of phenylacetylene in refluxing ethanol to give a 2/1 *E* : *Z* mixture of 1,4-diphenylbuten-3-ynes.

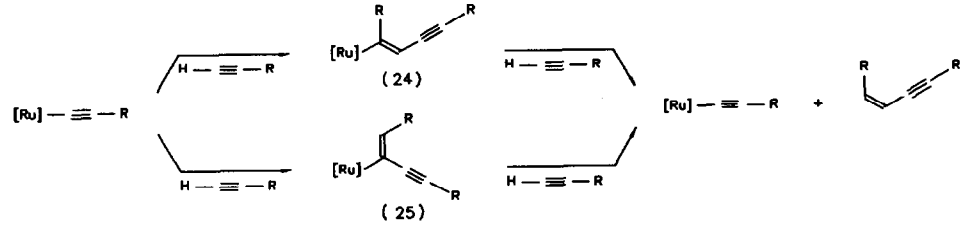


(7)

(22)

The formation of head-to-head dimer **22** may proceed through cleavage of the ruthenium–carbon bond of a butenynylruthenium complex (**24** or **25**) [12,17] provided in the reaction of the alkyne with a σ-alkynylruthenium derivative (Scheme 2). Further reaction of **24** or **25** with the 1-alkyne should regenerate the σ-alkynyl complex and formation of the (*Z*)-1,4-disubstituted butenyne.

The reported preparation of 1,4-diphenylbuta-1,3-diene under stoichiometric conditions takes place with regeneration of the hydride, suggesting that under the appropriate conditions a catalytic synthesis of dienes with ruthenium hydrides would be feasible. Further studies are in progress.



(24)

(25)

Scheme 2

Experimental

IR spectra were recorded on a Pye Unicam SP-3-300S spectrometer (only characteristic bands are given). ^{1}H NMR spectra were recorded on Bruker AM 200 (200 MHz) or Varian XL-300 (300 MHz) spectrometers with $CDCl_3$ solutions containing tetramethylsilane as internal standard. ^{2}H NMR spectrum was recorded at 46.4 MHz in a Varian XL-300 spectrometer with an spectral width of 3000 Hz. ^{13}C NMR spectra were recorded on a Bruker AM 200 (50 MHz) spectrometer in $CDCl_3$ with the solvent as internal standard. Carbon multiplicities were assigned by DEPT. Low resolution mass spectra (LRMS) were obtained with a VG-12-250 spectrometer.

Flash column chromatography was performed with Macherey Nagel 230-400 silica gel. Elemental analyses were performed at the Instituto de Química Orgánica. All reactions were carried out in pure solvents under N_2.

Ruthenium(II) hydrides **1** [3], **3** [5], **6** [7], **8** [8], and **21a,21b** [13] and alkenylruthenium(II) complexes **2** [5], **5** [6], **7** [8], **10** [9], **12** [8], **16** [5], **17,18** [6], and **19,20** [5] were prepared by known procedures.

*Synthesis of (*E,E*)-1,4-diphenylbuta-1,3-diene (4)*

A suspension of alkenyl complex **2** (371 mg, 0.43 mmol) in ethanol (15 mL) was heated under reflux for 30 h. The resulting suspension was filtered and the solid washed with ethanol, diethyl ether, and hexane, to give hydride **3** (280 mg, 85%), identical with an authentic sample [5]. The filtrate was evaporated and the residue was chromatographed (hexane) to yield **4** (40 mg, 91%) as a white solid, with spectral data identical with those previously reported [18]: IR (cm^{-1}): 3010, 1485, 1440, 990, 740, 690. ^{1}H NMR (300 MHz): δ 7.46–7.18 (m, 10H); 7.03–6.68 (m, 2H); 6.74–6.69 (m, 2H). ^{13}C NMR (DEPT): δ 137.4 (s); 132.8 (d); 129.3 (d); 128.6 (d); 127.6 (d); 126.4 (d). LRMS *m/z* 206 (M^+, 100%), 205 (41), 191 (40), 128 (38), 91 (40). Similar results were obtained from complexes **5** [6] or **7** [8].

Reaction of complex **7** (69 mg, 0.07 mmol) and 3,4-dimethoxybenzyl alcohol (32 mg, 0.19 mmol) in 1,2-dichloroethane (5 mL) under reflux for 3 h gave, after cooling to room temperature and evaporation of the solvent, a ca 1 : 1 mixture of hydride **8**, (identical with an authentic sample [8]) and 3,4-dimethoxybenzaldehyde (^{1}H NMR: δ 9.87 (CHO)).

*Synthesis of (*E*)-1,4-diphenyl-1-butene (9)*

A suspension of the alkenyl complex **2** (231 mg, 0.26 mmol) in ethanol (12 mL) was heated under reflux for 48 h and then cooled to room temperature. The precipitate of the hydride **3** (130 mg, 64%) was filtered off. The filtrate was evaporated and the residue chromatographed (hexane) to yield **9** (18 mg, 65%) as a white solid. M.p. 38 °C, lit. [19] 38 °C. IR (neat, cm^{-1}): 3050, 2950, 1550, 1490, 1440, 960, 735, 690. ^{1}H NMR (300 MHz): δ 7.34–7.18 (m, 10H); 6.41 (d, J = 15.9 Hz, 1H); 6.25 (dt, J = 15.9, 6.7 Hz, 1H); 2.81–2.76 (m, 2H); 2.56–2.49 (m, 2H). ^{13}C NMR: δ 141.76, 137.74, 130.39, 129.97, 128.47, 128.34, 126.92, 125.99, 125.88, 35.97, 34.84. LRMS: *m/z* 208 (M^+, 11), 118 (10), 117 (100), 115 (32), 91 (31), 77 (4).

Butene **9** was also prepared by heating a suspension of hydride **3** (201 mg, 0.26 mmol) and butadiene **4** (40 mg, 0.19 mmol) in ethanol (5 mL) for 21 h. The mixture was allowed to cool to room temperature and the hydride **3** (150 mg, 75%) filtered

off. The filtrate was evaporated and the residue chromatographed (hexane) to give **9** (20 mg, 50%).

*Synthesis of (*E,E*)-1,4-diphenylbuta-1,3-diene-2,3-d_2 (**14**)*

A solution of hydride **3** (350 mg, 0.45 mmol) and deuteriophenylacetylene (0.10 mL, 0.91 mmol) in dichloromethane (15 mL) was heated under reflux for 1 h. The mixture was allowed to cool to room temperature, then concentrated to ca 2 mL and diluted with diethyl ether. The yellow crystals formed were filtered off to yield ruthenium complex **13** (344 mg, 87%). ^{1}H NMR (200 MHz): δ 8.53 (d, $J = 5.0$ Hz, 2H, py); 7.53–7.42 (m, 12H, Ph); 7.25–7.06 (m, 21H, 18H Ph + 1H py + 2H PhC=C); 6.90 (t, $J = 7.1$ Hz, 1H, PhC=C); 6.85 (d, $J = 6.8$ Hz, 2H, PhC=C); 6.57 (t, $J = 6.8$ Hz, 2H, py); 5.80 (br s, 1H, CH=C). ^{13}C NMR showed a very broad resonance at δ 154 corresponding to *C*D=DHPh (the parent alkenyl complex showed a triplet at 53.77 ppm [5]).

A suspension of alkenyl complex **13** (318 mg, 0.36 mmol) in ethanol (10 mL) was heated under reflux for 13 h, then allowed to cool to room temperature. The solid was filtered off and shown to be the pure hydride **3** (225 g, 80%). The filtrate was evaporated and the residue chromatographed (hexane) to yield **14** (25 mg, 65%): ^{1}H NMR (200 MHz): δ 7.46–7.18 (m, 10H); 6.70–6.62 (m, 2H). LRMS: *m/z* 208 (M^+, 100), 207 (92), 192 (32), 130 (34), 92 (42).

Synthesis of trans*-stilbene (**11**) from alkenyl complex **10***

A suspension of alkenyl complex **10** (146 mg, 0.17 mmol) and triphenylphosphine (44 mg, 0.17 mmol) in ethanol (14 ml) was heated under reflux for 20 h, then allowed to cool to room temperature and concentrated to ca 3 mL. The solid was filtered off and shown to be the hydride **1** (60 mg, 38%). The filtrate was evaporated and the residue chromatographed (hexane) to give *trans*-stilbene (**11**) (25 mg, 83%) as a white crystalline solid, identical with an authentic sample. ^{1}H NMR (300 MHz): δ 7.53–7.50 (m, 4H); 7.38–7.33 (m, 4H); 7.28–7.23 (m, 2H); 7.11 (s, 2H).

Synthesis of trans*-stilbene (**11**) from alkenyl complex **12***

A suspension of alkenyl complex **12** (554 mg, 0.523 mmol) in ethanol was heated under reflux for 4.5 h, then allowed to cool to room temperature. The solid was filtered off and shown to be the hydride **8** (340 mg, 73%). The filtrate was evaporated and the residue chromatographed (hexane) to give **11** (67 mg, 71%).

Similarly, reaction of **12** (104 mg, 0.10 mmol) in methanol-d_4 (99.8% D, 1 mL) in a sealed tube at 80 °C for 3 h gave deuteride **8**-*d* (isolated as a white solid, 25 mg, 23%). ^{2}H NMR (46.4 MHz, $CHCl_3$ with $CDCl_3$ as internal reference): δ −12.90 (br t, $J = 3$ Hz). Evaporation of the solvent gave deuterated *trans*-stilbene (15 mg, 85%). LRMS (only the higher mass peaks are given): *m/z* 183 (10), 182 (66), 181 (100), 180 (89), 179 (56), 178 (23), 177 (9), 176 (4).

Catalytic dimerization of phenylacetylene

A suspension of hydride **21a** (80 mg, 0.09 mmol) in phenylacetylene (1.0 mL, 9.11 mmol) was heated at 100 °C in the presence of 2,6-di-t-butyl-4-methylphenol (BHT) (ca 2 mg) for 20 h. The mixture was then cooled to room temperature and evaporated, and the residue was chromatographed (hexane) to give (*Z*)-1,4-diphenylbuten-3-yne (**22**) [15,16] as an oil (200 mg, 21%). IR (neat, cm^{-1}): 2120, 1600, 780,

690. ^{1}H NMR (300 MHz): δ 7.93–7.89 (m, 2H); 7.49–7.46 (m, 2H); 7.38–7.28 (m, 6H); 6.67 (d, $J = 11.9$ Hz, 1H); 5.90 (d, $J = 11.9$ Hz, 1H). ^{13}C NMR: δ 138.6, 136.6, 131.4, 128.7, 128.5, 128.4, 128.3, 128.2, 107.4, 95.8, 88.3. LRMS: *m/z* 204 (M^+, 100), 203 (80), 202 (69). Longer reaction times afforded a mixture of *E* and *Z* isomers; (*E*)-1,4-diphenylbuten-3-yne: ^{1}H NMR (200 MHz) (only characteristic signals): δ 7.12 (d, $J = 16.4$ Hz, 1H); 6.45 (d, $J = 16.4$ Hz, 1H).

[Ru(CO)H(C_5H_5N)(CN^{t}Bu) (PPh_3)$_2$]PF_6 (23)

To a suspension of [Ru(CO)H(CD_5H_5N)$_2$(PPh_3)$_2$]PF_6 (**21b**) (200 mg, 0.21 mmol) in ethanol (25 mL) at 23°C was added t-butyl isocyanide (0.026 mL, 0.23 mmol) at 23°C. The mixture was stirred at this temperature for 24 h, then filtered to yield a grey solid, which was washed with diethyl ether and hexane to yield the pale grey **23** (159 mg, 79%). IR (cm^{-1}): ν(C≡N) 2155s, ν(C≡O) 1975vs, ν(Ru–H) 1880vw, ν(C=N) 1600w, ν(PF_6) 840vs. ^{1}H NMR (300 MHz): δ 7.86–7.75 (m, 2H, py); 7.46–7.22 (m, 33H, PPh_3 + 3H py); 1.22 (s, 9H), −6.22 (t, $J = 18.0$ Hz, 1H). Anal. Found: C, 58.35; H, 5.01; N, 3.15. $C_{47}H_{45}F_6N_2OP_3Ru$ calc.: C, 58.69; H, 4.72; N, 2.91%.

Acknowledgments

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