Organometallics **2002,** *21,* 2572−2574

Communications

Novel Metallacycle Complexes from Bis(oxazolinyl)pyridine−Rhodium(I) Species and Diynes

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Received March 25, 2002

Summary: The reaction of $[Rh(coe)_2Cl]_2$ *(coe = cis-cyclooctene), bis(oxazolinyl)pyridine (pybox), and diynes* $(O(CH_2C{\equiv}CCO_2Me)_2$ *and* $PhC{\equiv}CCH_2OCH_2C{\equiv}CCO_2Me)$ *gave new types of metallacycle complexes, which were analyzed by X-ray crystallography and showed catalytic activity for cycloaddition of diynes and several alkynes.*

Metallacycle complexes have been intensively studied as important intermediates for the cyclotrimerization of alkynes and/or diynes in terms of mechanistic view and discovery of new efficient catalysts.[1−3] In the course of our research on nitrogen-based ligands and catalytic reactions with their transition-metal complexes,[4] we found that the oxidative addition reaction of alkyl chlorides (e.g. CH_2Cl_2 and $ClCH_2CO_2Me$) to pybox−Rh^I-Cl species generated *in situ* from pybox and $[Rh(coe)_2Cl]_2$ proceeds to form stable pybox−Rh^{III}−alkyl complexes.[5a] In this context, the existence of such rhodium(I) species with certain tridentate nitrogen ligands (κ^3-N,N,N type) has recently been proved by isolation and X-ray analysis by other chemists.[3b,c,h] On the basis of these findings, we thought that diynes could add to the *in situ* pybox−Rh^ICl species to oxidatively cyclize and to give new types of metallacycles, pybox−rhodacyclopentadienes.

The reaction of pybox-*dh* and $[Rh(coe)_2Cl]_2$ (2:1 mol ratio) with the diyne **1** was carried out in an absolute tetrahydrofuran (THF) solution at 25−30 °C for 17 h. Chromatographic separation of the reaction residue gave thermally stable orange solids, which proved to be the corresponding rhodacycle complex **2**, in 68% yield (Scheme 1).[6] Structural elucidation of **2** was performed by NMR spectroscopy and X-ray crystallographic analysis (Figure 1). The complex **2** has an octahedral configuration with the rhodacyclopentadiene skeleton, where the two carbon atoms (C1 and C4) are located at an equatorial position and an axial position, respectively. The rhodacycle moiety also proved to be a typical metallacyclopentadiene,[1b−d] not a metallacyclopentatriene, as postulated for some ruthenium complexes:[7] 2.0 Å, Rh−C1; 1.34 Å, C1−C2; 1.44 Å, C2−C3; 1.35 Å, C3−C4; 2.04 Å, C4−Rh; 80.5°, C1−Rh−C4.[1b−d] The two methoxycarbonyl groups of **2** are located just filling the spaces over the pybox plane and by the side of the chloride atom, respectively. Accordingly,

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10.1021/om0202221 CCC: $22.00
Publication on Web 05/29/2002

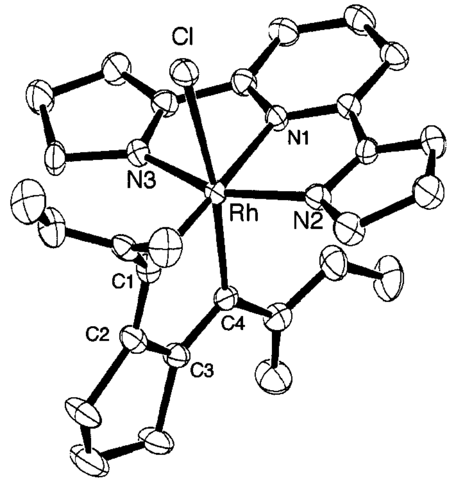
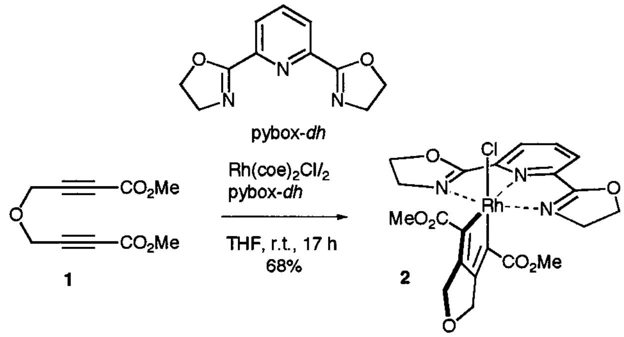


Figure 1. Molecular structure of the pybox–rhodacycle complex **2** showing 30% thermal ellipsoids.

Scheme 1



one of the proton signals for the methoxy groups appears at higher magnetic field by the shielding effect of the pybox plane: for two CH_3O, δ 3.23 and 3.82 ppm.

We attempted in turn the catalytic cycloaddition of the diyne **1** and some alkynes, such as phenylacetylene, 1-hexyne, and (trimethylsilyl)acetylene, by using the complex **2** (5 mol %) as a catalyst. Although the oxidative cyclization of the diyne giving **2** took place at room temperature, the cycloaddition process needed higher temperature to give the corresponding adducts **3**–**5** in good yields (Scheme 2, Table 1); no reaction occurs below 60 °C. A 7–10-fold excess of alkynes is necessary to obtain higher yields in order to decrease (1) self-trimerization of alkynes **3**–**5** and (2) formation of 2 + 1 adducts of alkyne/diyne or diyne/alkyne. As alkynes, dimethyl acetylenedicarboxylate and methyl propiolate were employed, but not to give the corresponding adducts by formation of their trimers and some amounts of the 2 + 1 adducts. Alternatively, an *in situ* catalyst, the mixture of pybox-*dh* and $[Rh(coe)_2Cl]_2$, was also applicable for this purpose to give similar results (runs 6 and 7).

Scheme 2

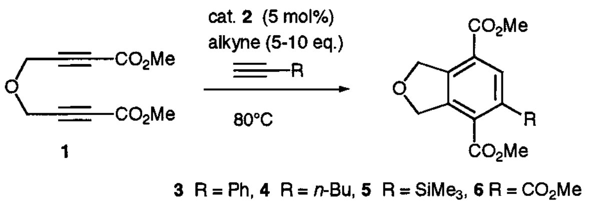
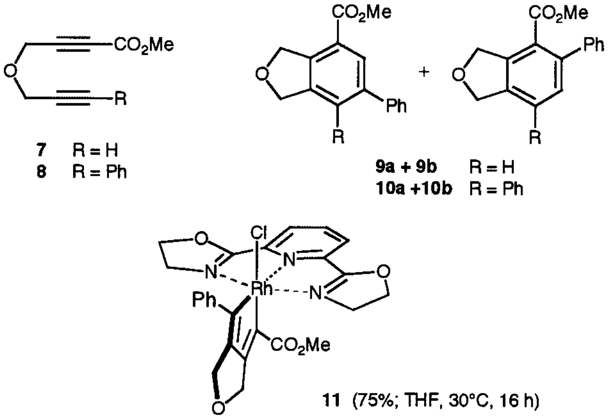


Table 1. Cycloaddition of Diyne 1 and Alkynes with Pybox–Rh Catalysts[a]

run no.	cat.	alkyne R (amt, equiv[d])	time (h)	product	yield[b] (%)
1	**2**	Ph (5)	4	**3**	74
2	**2**	Ph (10)	2	**3**	84
3	**2**	*n*-Bu (7)	30	**4**	68
4	**2**	$SiMe_3$ (7)	72	**5**	47
5	**2**	CO_2Me (7)	24	**6**	0
6	*in situ*[c]	Ph (7)	5	**3**	72
7	*in situ*[c]	$SiMe_3$ (7)	72	**5**	23

[a] Conditions: **1** (0.2 mmol), **2** (0.01 mmol), chlorobenzene (2 mL). [b] Isolated yield based on **1**. The dimer of the diyne was obtained in ca. 5–20% yield. [c] In situ catalyst prepared by mixing of pybox-*dh* (0.015 mmol) and $[Rh(coe)_2Cl]_2$ (0.005 mmol) in chlorobenzene (2 mL). [d] With respect to **1**.

Chart 1



In the reaction of the diyne monoester **7** (0.2 mmol; Chart 1) and phenylacetylene (2.0 mmol), the catalytic cycloaddition using **2** (5 mol %) proceeded smoothly at 80 °C in chlorobenzene for 2 h to give the adduct **9** in 95% yield, but as a mixture of the regioisomer **9a** + **9b** (63:37 ratio of the isomer). In this system, the corresponding metallacycle complex could not be isolated at ambient temperature, probably because of its unstability.

On the other hand, it is worthy of note that the phenyl–diyne–monoester **8** reacted with *in situ* pybox–Rh species in a manner similar to the preparation of **2** to give the rhodacycle complex **11** in 75% (purified yield) as a sole product.[8] No stereoisomer was detected, even in the crude product, by ^1H NMR. Interestingly, the

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(6) Complex **2**: orange-red solid, dec pt 233–235 °C. IR (KBr): ν 1686, 1680 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 3.23 (s, 3 H), 3.78 (m, 2 H), 3.82 (s, 3 H), 4.03 (m, 2 H), 4.62 (s, 2 H, OCH_2), 4.70 (s, 2 H, OCH_2), 4.93 (t, $J = 9.9$ Hz, 4 H, OCH_2), 7.94 (d, $J = 7.8$ Hz), 8.19 (t, $J = 7.8$ Hz × 2). ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si): δ 50.40, 50.81, 51.39 (d, $J = 1.4$ Hz), 66.92, 70.51, 72.69, 124.37, 125.89 (d, $J = 35.5$ Hz), 138.16, 144.37, 155.26, 160.68 (d, $J = 31.2$ Hz), 166.68 (d, $J = 1.7$ Hz), 169.70 (d, $J = 1.4$ Hz), 174.86, 175.37. X-ray analysis: a single crystal (0.15 × 0.3 × 0.4 mm) was obtained by recrystallization from CH_2Cl_2–*n*-hexane. Crystal data: $C_{21}H_{21}N_3O_7ClRh$, monoclinic, space group $P2_1/n$ (No. 14), $a = 10.492(3)$ Å, $b = 12.290(3)$ Å, $c = 17.481(4)$ Å, $\beta = 102.61(1)°$, $V = 2199.6(7)$ Å^3, $\rho_{calcd} = 1.708$ g cm^{-3}, $Z = 4$, $\mu = 9.45$ cm^{-1}. The intensity data ($2\theta < 55.1°$) were collected on a Rigaku AFC-7R diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å) and the structure was solved by direct methods (SIR88). The final cycle of refinement was based on 3098 observed reflection ($I > 3.00\sigma(I)$) and 298 variable parameters and converged with $R = 4.4\%$ and $R_w = 5.0\%$. The Cambridge Crystallographic Database file is CCDC-178534.

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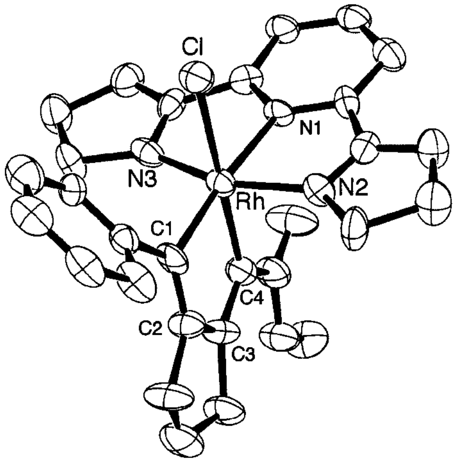
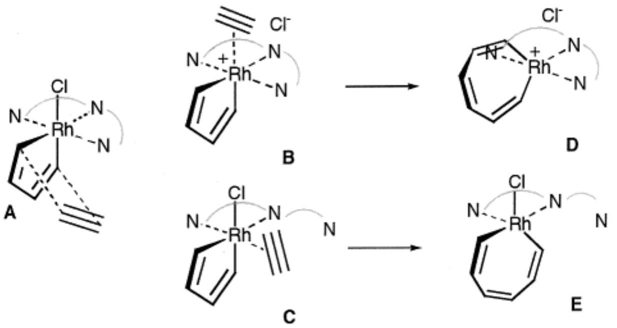


Figure 2. Molecular structure of the pybox−rhodacycle complex **11** showing 30% thermal ellipsoids.

Scheme 3



X-ray analysis of **11** shows that the carbon atom (C4) bound to the ester part on the diyne skeleton is located at the apical position, while the carbon atom (C1) bound to the phenyl group is placed at the equatorial position (Figure 2): 2.05 Å, Rh−C1; 1.30 Å, C1−C2; 1.43 Å, C2−C3; 1.38 Å, C3−C4; 2.03 Å, C4−Rh; 78.7°, C1−Rh−C4. Nevertheless, the cycloaddition of the diyne **8** and phenylacetylene catalyzed by the complexes **11** (5 mol %) in benzene at 80 °C resulted in nonstereoselective formation of the adduct **10a** + **10b**, in 72% yield (51:49).

Although we cannot elucidate the mechanism and nonstereoselectivity at this stage, we hypothesize that the cycloaddition concertedly proceeds via direct attack of alkyne at the diene moiety of the rhodacycle skeleton, having a 18-electron coordinatively saturated trivalent rhodium atom (**A**; Scheme 3), followed by reductive elimination, releasing the adduct and active pybox−Rh^{I}-Cl species. Other possibilities, such as alkyne insertion on the cationic and unsaturated alkyne complexes (**B** and **C**) to form the rhodacycloheptatrienes (**D** and **E**, respectively), remain unsolved.[9]

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan (Tokutei A, 412).

Supporting Information Available: Text giving synthetic procedures for the complexes **2** and **11** and selected catalytic procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0202221

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(8) Complex **11**: orange-red solid, dec pt >250 °C. IR (KBr): ν 1660 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2, Me_4Si): δ 3.18 (s, 3 H), 3.8−4.0 (m, 2 H), 4.60 (s, 2 H, OCH_2), 4.72 (s, 2 H, OCH_2), 4.94 (t, J = 10.0 Hz × 2, 4 H, OCH_2), 7.16 (t, J = 7.2 Hz × 2, 1H), 7.30 (t, J = 7.2 Hz × 2, 2H), 7.41 (d, J = 7.2 H, 2H), 7.97 (d, J = 8.0 Hz), 8.17 (t, J = 8.0 Hz × 2). ^{13}C NMR (100 MHz, CD_2Cl_2, Me_4Si): δ 50.23, 52.25, 67.59, 70.76, 73.04, 122.73 (d, J = 35.5 Hz), 124.49, 124.99, 127.10, 127.80, 138.27, 144.72, 149.54, 153.57, 167.40, 170.42, 175.31, 175.31, 178.57 (d, J = 30.0 Hz). X-ray analysis: a single crystal (0.1 × 0.4 × 0.5 mm) was obtained by recrystallization from benzene−ether−hexane−CH_2Cl_2. Crystal data: $C_{35}H_{35}N_3O_6ClRh$, monoclinic, space group $P2_1/n$ (No. 14), $a = 12.229(4)$ Å, $b = 21.324(5)$ Å, $c = 13.355(4)$ Å, $\beta = 97.58(2)°$, $V = 3452(1)$ Å^3, $\rho_{calcd} = 1.408$ g cm^{-3}, $Z = 4$, $\mu = 6.18$ cm^{-1}. The crystal contains a 1:1:1 mole ratio of **11**, benzene, and ether; the solvent molecules in the crystal were omitted in Figure 2. The intensity data ($2\theta < 55.1°$) were collected on a Rigaku AFC-7R diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 69$ Å), and the structure was solved by Patterson methods (DIRDIF92, PATTY). The final cycle of refinement was based on 2140 observed reflections ($I > 3.00\sigma(I)$) and 360 variable parameters and converged with $R = 6.9\%$ and $R_w = 8.0\%$. The Cambridge Crystallographic Database file is CCDC-178535.

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