Mesoionic Carbenes: Reactions of 1,3-Diphenyltetrazol-5-ylidene with Electron-Deficient Alkenes, and Synthesis and Catalytic Activities of the (Tetrazol-5-ylidene)rhodium(I) Complexes

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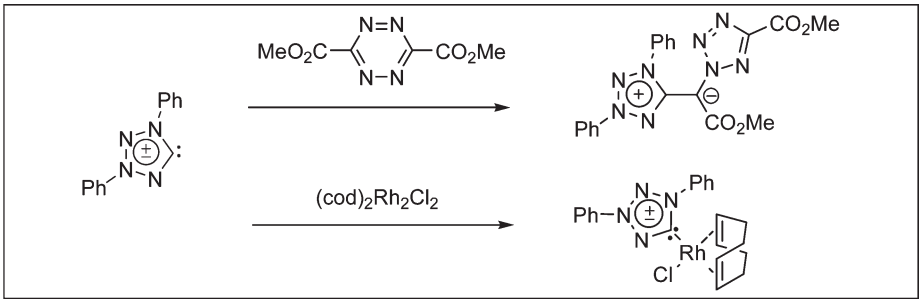

The reactions of 1,3-diphenyltetrazol-5-ylidene, a rare example of mesoionic carbenes, with electron-deficient unsaturated compounds were studied. The carbene reacted with dimethyl 1,2,4,5-tetrazine-3, 6-dicarboxylate to give a 5-tetrazoliomethylide, together with hydrazine derivatives. The reaction with tetracyanoethylene gave another methylide in low yield. On the contrary, the reactions with weaker electrophiles, such as 3,6-diphenyl-1,2,4,5-tetrazine, fumalonitrile, *N*-phenylmaleimide, and dimethyl acetylenedicarboxylate, did not give any coupling products, but gave phenylated products and/or Michael addition products *via* the degradation of the 1,3-diphenyltetrazole ring. Novel mesoionic mono- and bis(carbene)-rhodium(I) complexes were synthesized and the structures were characterized by X-ray crystallography. Their catalytic activities for the decarbonylative addition reaction of benzoyl chloride to ethynylbenzene were investigated.

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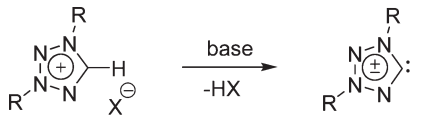
INTRODUCTION

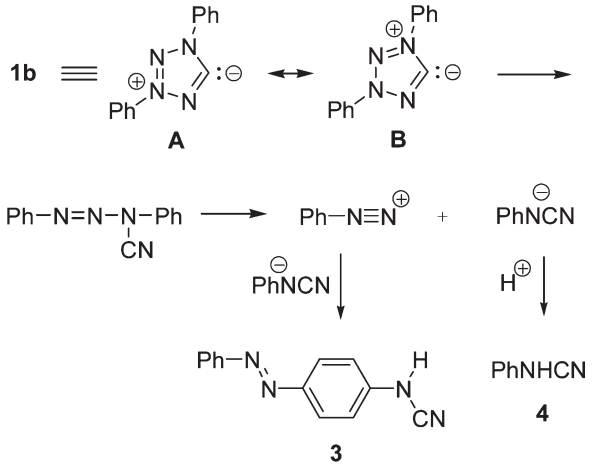
Since the Arduengo's pioneering work on stable heterocyclic carbenes, various heterocyclic carbenes, including *N*-heterocyclic carbenes (NHCs) such as imidazol-2-ylidene and 1,2,4-triazol-3-ylidene, have hitherto been prepared and their physical and chemical properties have intensively been investigated [1]. Mesoionic compounds are the unique family of heterocycles owing to their interesting electronic nature; *i.e.*, they cannot be formulated satisfactorily by a single covalent or polar structure, but expressed as a resonance hybrid of a series of dipolar canonical structures [2]. Mesoionic carbenes, which are derived formally from mesoionic compounds by a removal of the exo-cyclic atom(s), are also resonance hybrids of several canonical structures. Contrary to the extensive study on NHCs, mesoionic carbenes are scarecely studied. 1,3-Dimethyl- (**1a**) and 1,3-diphenyltetrazol-5-ylidene (**1b**) are rare examples of such mesoionic carbenes. These carbenes are easily prepared by deprotonation of the corresponding 1,3-disubstituted tetrazolium salts **2a**,**b** with a base at low temperature [3,4]. Alternatively, **1b** can also be generated by the reaction of 5-azido-1,3-diphenyltetrazolium salt with sodium azide [5]. Carbene **1** is thermally labile; upon warming to room temperature, **1** undergoes a ring-opening to give 3-cyanotriazene. In the case of **1b**, further degradation and recombination reactions occur spontaneously to give 4-(phenylazo)phenylcyanamide (**3**) and phenylcyanamide (**4**) (Scheme 1) [6]. As an isomeric carbene of **1**, 2,3-diphenyltetrazol-5-ylidene (**5**) is also known, which is generated similarly by deprotonation of 2,3-diphenyltetrazolium salts [7]. This mesoionic carbene is also unstable to give cyanoazimine **6** (Scheme 2). Although various stable NHCs have recently been attracting increasing interest, only these two examples **1** and **5** of mesoionic carbenes are thus far synthesized.



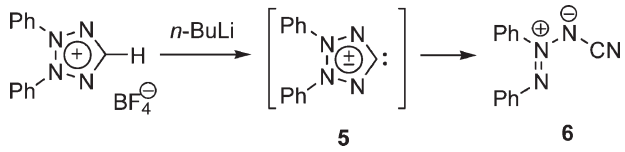
2a R=Me
2b Ph

1a R=Me
1b Ph

Scheme 1



Scheme 2



Our previous work demonstrated that carbene **1b** has a nucleophilic nature and hence is best expressed by the singlet structures **A** and **B**. For example, although the attempted reactions with alkyl halides or carbonyl compounds were unsuccessful, **1b** reacts readily with nitrogen electrophiles such as benzenediazonium and azidotetrazolium salts [4,5]. Here, we report further reactions of **1b** with electron-deficient tetrazine and alkene electrophiles. Furthermore, the synthesis and characterization of stable rhodium(I) complexes of **1b** are disclosed as examples of transition-metal complexes of mesoionic carbenes.

RESULTS AND DISCUSSION

A. Reaction with 1,2,4,5-tetrazines. It is reported that 1,2,4-triazol-3-ylidene reacts with 3,6-diphenyl-1,2,4,5-tetrazine to give a [4+1] cycloaddition product [8]. We attempted the reaction of **1b** with 3,6-diphenyl-1,2,4,5-tetrazine. However, no reaction occurred and only the degradation products **3** and **4** were obtained. Next, dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate **8**, a more electron-poor tetrazine bearing the electron-withdrawing substituents, was employed. The carbene **1b** was generated *in situ* from the tetrazolium salt **2b** and reacted with **8** under different reaction conditions, by changing the solvent and the reaction temperature. These results are summarized in Table 1.

Three products **9**, **10**, and **11** have been isolated from the reaction mixtures in varying yields, together with small amounts of olate **7** and **4** (Scheme 3). Olate **7** is considered to be formed by the reaction of **1b** with atmospheric oxygen [4]. The compound **9** has been revealed to be a 1:1 adduct of **1b** and **8** on the basis of the MS and elemental analyses. A characteristic signal at 78.7 ppm in the ^{13}C NMR spectrum suggests that this compound is a 5-tetrazoliomethylide derivative [9]. The structure was finally comfirmed by X-ray chrystallography (Fig. 1). The exo-cyclic methylide C—C—N plane and the tetrazolium ring share almost the same plane. The phenyl ring at N^3 lies in this plane; on the contrary, the phenyl ring at N^1 as well as the tetrazole ring attached to the methylide carbon tilt considerably. The pivotal carbon—carbon bond length is 1.406(3) Å, indicating a mixed nature of single and double bonds. Compound **10** has a molecular formula $C_{19}H_{16}N_6O_4$, which corresponds to a loss of N_2 from the sum of **1b** and **8**. ^1H and ^{13}C NMR data show that **10** has a *p*-substituted benzene ring and two inequivalent CO_2Me groups. The structure was eventually deduced to be 4-(*p*-phenylazo) phenylhydrazone of a pyrazolone derivative. Compound **11** has a structure similar to **10**, bearing an unsubstituted phenylhydrazone moiety. An attempted reaction of **11** with benzene-diazonium salt did not give **10**. This fact suggests that **10** might be formed *via* an intramolecular migration of the phenylazo group. The most plausible mechanism for the formation of compounds **9**, **10**, and **11** is shown in Scheme 4.

A nucleophilic attack of **1b** to the electron-deficient carbon of tetrazine **8** followed by a ring-contraction

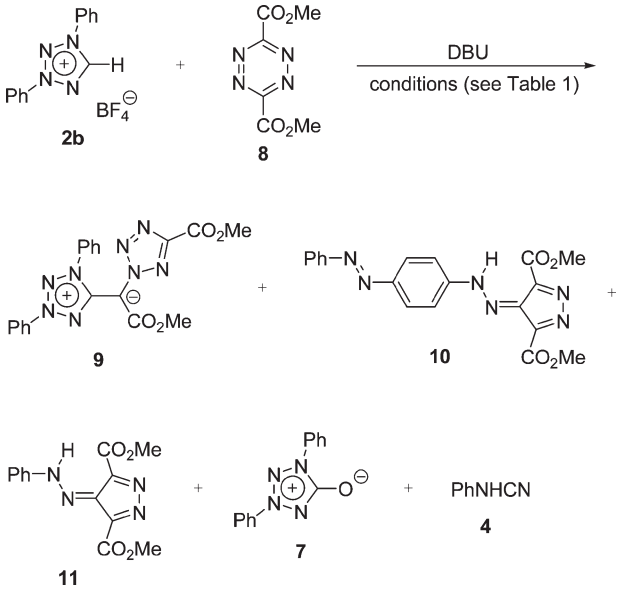
Table 1

The reaction of mesoionic carbene **1b** with **8**.

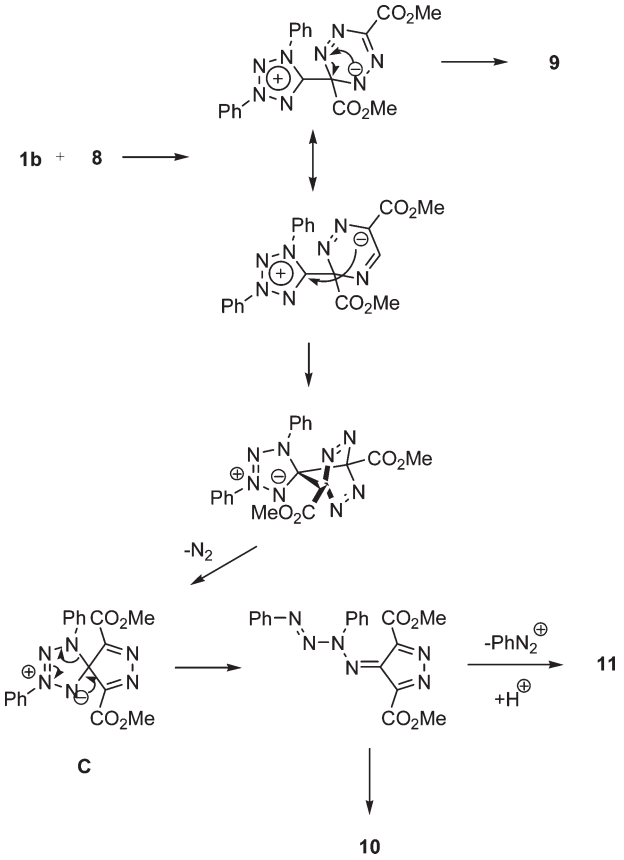
Entry	Temperature	Solvent	*t* (h)	Yield (%)				
				9	**10**	**11**	**7**	**4**
1	−20°C to r.t.	DMA	3	Trace	6[a]	24[a]	8	18
2	−20°C to r.t.	DMF	3	2[a]	7[a]	37[a]	3	5
3	−60°C to r.t.	DMF	4	15[a]	4[a]	22[a]	2	8

[a] Determined by ^1H NMR.

Scheme 3



Scheme 4



furnishes **9**. Compounds **10** and **11** are considered to be formed *via* the spiro intermediate **C** which is akin to the product of the reaction of 1,2,4-triazol-3-ylidene and diphenyltetrazine [8]. The cleavage of the tetrazole ring of **C** followed by an intramolecular migration of the phenylazo group (aza para-Claisen rearrangement) gives **10**, whereas a loss of the phenylazo group furnishes **11**. Now it has been found that carbene **1b** reacts readily with the electron-deficient unsaturated compound. Then, the reactions of **1b** with alkenes with electron-withdrawing groups were next undertaken.

B. Reaction with tetracyanoethylene. A mixture of the tetrazolium salt **2b** and tetracyanoethylene was treated with DBU at –60°C, and the mixture was warmed to room temperature. The reaction gave a complex mixture of products, from which only cyanomethylide **12** was isolated as stable yellow crystals in low yield (9%) after column chromatography. The formation of **12** is rationalized by Scheme 5. The initially formed Michael adduct is considered to undergo a cyano group migration to furnish the fully conjugated methylide **12**.

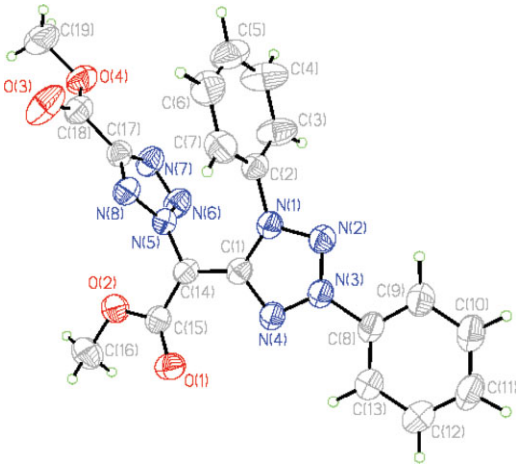
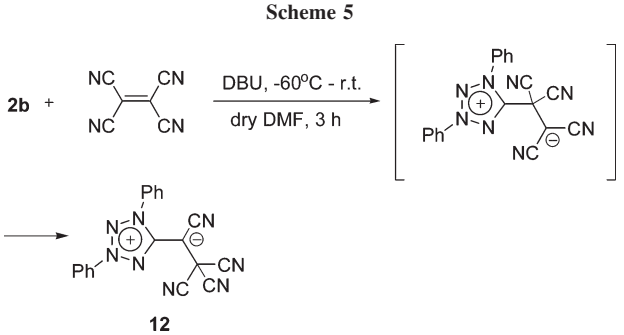


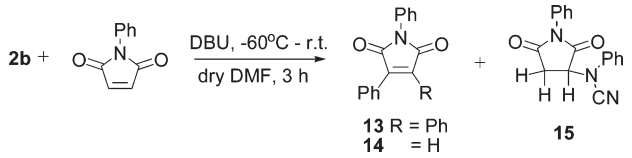
Figure 1. Molecular structure of methylide **9**. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

C. Reaction with *N*-phenylmaleimide, fumalonitrile, and dimethyl acetylenedicarboxylate. The reaction of mesoionic carbene **1b** with *N*-phenylmaleimide at –60°C to room temperature gave phenylated maleimides **13** and **14** together with cyanamide **15** (Scheme 6). To determine the origin of the phenyl group of **13** and **14**,

Scheme 5



Scheme 6

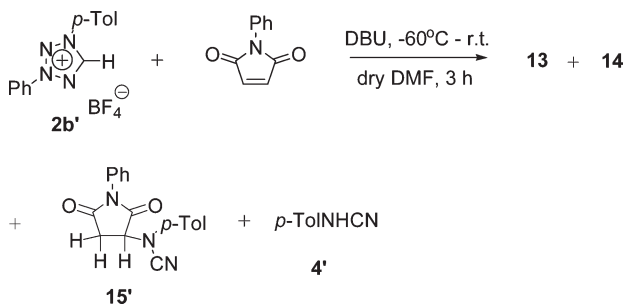


1-(*p*-tolyl)-3-phenyltetrazolium **2b′** was employed in place of **2b**. The reaction gave **13** and **14**, and the *p*-tolylcyanamide adduct **15′**. *p*-Tolylcyanamide **4′** itself was also isolated (Scheme 7). On the basis of these results, a plausible reaction mechanism is illustrated in Scheme 8. Carbene **1b** decomposes thermally to give benzendiazonium cation and phenylcyanamide anion; the former is considered to give phenyl radical [10] which reacts with *N*-phenylmaleimide to furnish the phenylated compounds **13** and **14**. The phenylcyanamide anion gives the adduct **15** *via* the Michael addition to *N*-phenylmaleimide.

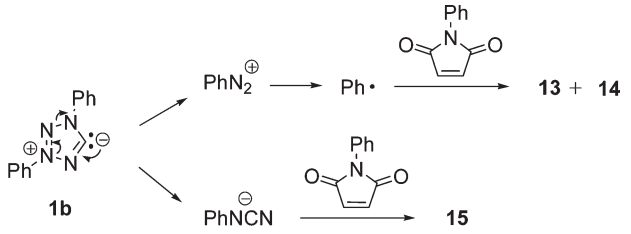
The reaction of **1b** with fumalonitrile also gave the phenylation products **16**, **17**, and **18** in low yields, together with the degradation products **3** and **4**. The reaction with dimethyl acetylenedicarboxylate gave the addition product **19** in 29% yield *via* a similar mechanism to the *N*-phenylmaleimide case (Scheme 9).

D. Preparation and characterization of rhodium(I) complexes of 1,3-diphenyltetrazol-5-ylidene. It is well known that carbenes can be stabilized by complexation with metals. Indeed, a large number of main group metal as well as transition metal complexes of NHCs have hitherto been prepared and characterized. Of such NHCs, imidazol-2-ylidene [11] and 1,2,4-triazol-3-ylidene [12] are most extensively studied, and some imidazol-2-ylidene-metal complexes have been used as effective catalysts in organic syntheses [13]. On the other hand, very few examples of mesoionic carbene-metal complexes, such as mercury(II) and palladium(II) complexes, have been synthesized by us [4]. Here, we describe the preparation and characterization of rhodium(I) complexes of **1b** as a new entry of mesoionic carbene-metal complexes.

Scheme 7



Scheme 8

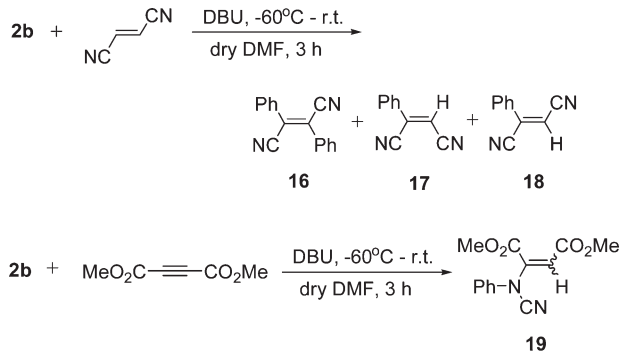


The reactions of tetrazolium salt **2b** with bis(1,5-cyclooctadiene)-μ,μ′-dichlorodirhodium (**20**) in DMF mediated by DBU were performed under various conditions. Two products, namely, mono- **21** and bis(tetrazol-5-ylidene)rhodium(I) complexes **22**, were isolated as stable crystalline solids (Scheme 10, Table 2). When an excess tetrazolium salt **2b** was used **22** was formed exclusively. Obviously, the cationic bis-carbene complex **22** is formed *via* the neutral mono-carbene complex **21**. Indeed, the reaction of **21** with **2b**/DBU gave **22**.

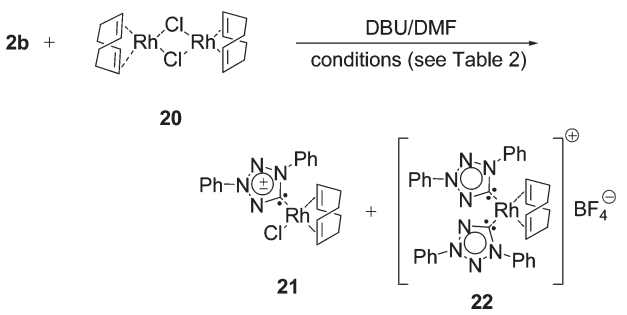
The molecular structures of the rhodium(I) complexes **21** and **22** were analyzed by X-ray crystallography (Figs. 2 and 3). In the square planner complex **21**, the tetrazol-5-ylidene ring is twisted relative to the coordination plane. The bond angle C(carbene)-Rh-Cl is 90.59(8)°. The C(carbene)-Rh length [2.017(3) Å] is almost coincident to that of (imidazol-2-ylidene)rhodium complex [11] [2.023(2) Å] and somewhat longer than that of (1,2,4-triazol-3-ylidene)rhodium complex [12(a)] [2.004 (7) Å]. The cationic bis(tetrazol-5-ylidene) complex **22** is also square planner. The bond angle C(carbene)-Rh-C(carbene) is 90.47(13)°. The C(carbene)-Rh lengths [2.039(3) and 2.031(3) Å] are longer than that of **21**, whereas they are shorter than the averaged length (2.047 Å) of the corresponding (imidazol-2-ylidene)rhodium complex [11].

To evaluate the catalytic activities, the complexes **21** and **22** were subjected to the decarbonylative addition reaction of benzoyl chloride to ethynylbenzene. The reaction is known to give (*Z*)-1-chloro-1,2-diphenylethene (**23**) by the catalysis of the $(cod)_2Rh_2Cl_2$ (**20**)

Scheme 9



Scheme 10



[14]. The mono(tetrazol-5-ylidene)Rh complex **21** (10 mol%) was found to be as effective as **20** to give **23** in 61% yield (Scheme 11). On the contrary, the bis (tetrazol-5-ylidene) complex **22** is less reactive to give lower yield (22%) of **23**, probably owing to the steric crowding around the rhodium atom.

CONCLUSION

The nucleophilic nature of 1,3-diphenyltetrazol-5-ylidene **1b** was demonstrated in the reactions with the electron-deficient tetrazine and alkene to yield the new 5-tetrazoliomethylide compounds **9** and **12**. In the cases of weak electrophiles, the degradation of the tetrazole ring took place and the phenylated products were obtained. Two (tetrazol-5-ylidene)rhodium(I) complexes **21** and **22** were synthesized *via* a nucleophilic displacement of the chlorine atoms of **20** with **1b**. Catalytic activities of **21** and **22** were investigated for the chloroarylation of ethynylbenzene. Further catalytic properties of these new rhodium complexes are now under way.

EXPERIMENTAL

Melting points were measured with a hot-stage apparatus and are uncorrected. Elemental analyses were carried with a Perkin–Elmer 2400 II CHNS/O. IR spectra were taken as KBr discs on a JASCO A-102 spectrometer. Electronic spectra were measured on a U-3500 spectrophotometer. ^{1}H NMR spectra were obtained using a Varian Gemini 200 (200 MHz) or a Varian Gemini 300 (300 MHz), and ^{13}C NMR spectra were obtained using a Varian Gemini-200 (50 MHz). Chemical shifts are recorded in ppm downfield from tetramethylsilane. *J* values are given in Hz. Mass spectra were taken with a Hitachi M-2000 spectrometer (EI, 70 eV). For TLC, Merck Silica gel 60 F_{254} Plate and Fuji Silysia Chemical Ltd. NH TLC Plate were used. For column chromatography, Merck Silica gel 60 (0.063–0.200 mm) and Fuji Silysia Chemical Ltd. Chromatorex NH Chromatography Silica Gel (100–200 mesh) were used.

Table 2

The reaction of tetrazolium salt **2b** with **20**.

Entry	**2b** (mmol)	**20** (mmol)	Conditions	Yield (%) **21**	**22**
1	0.50	0.25	−60°C, 3 h	12	31
2	0.25	0.25	0°C, 3 h	30	13
3	0.25	0.25	−60°C, 3 h	31	26
4	0.25	0.25	−60°C, 25 h	53	17
5	0.50	0.13	−60°C, 18 h	Trace	99

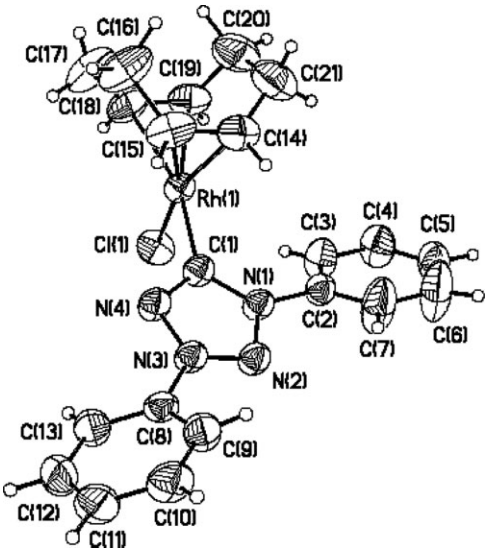


Figure 2. Molecular structure of the (tetrazol-5-ylidene)rhodium complex **21**.

Although no problems were hitherto encountered, it should be noted that polyaza compounds may in general be explosive and should be handled with due care.

Reaction with dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate (8).

Typical procedure. To a solution of **2b** (1.6 g, 5.0 mmol) and **8** (0.99 g, 5.0 mmol) in dry DMF (20 mL), DBU (0.75 mL, 5.0 mmol) was added at −60°C, and the mixture was warmed gradually to room temperature during a period of 4 h (Table 1, entry 3). Water was added and the precipitated

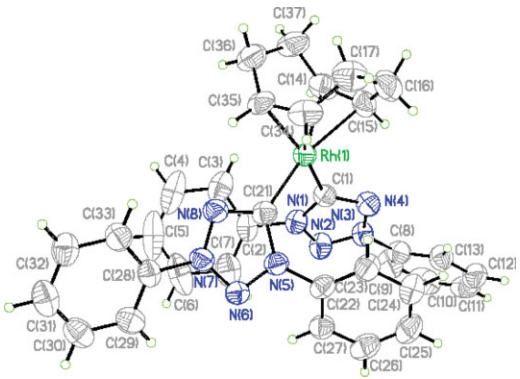
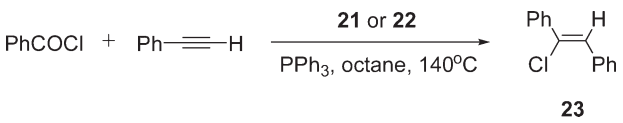


Figure 3. Molecular structure of the bis(tetrazol-5-ylidene)rhodium complex **22**. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Scheme 11



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solid was filtered off. The products were extracted from the filtrate with dichloro-methane. The extracts were dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue (reddish brown solid, 1.0 g) was chromatographed (SiO_2/CH_2Cl_2:EtOAc gradient and MeOH) to give **4** (49 mg, 8%), **7** (26 mg, 2%), and a mixture of **9**, **10**, and **11** (0.72 g). On the basis of the ^{1}H NMR analysis, the yields were estimated to be **9** (15%), **10** (4%), and **11** (22%). Pure samples of **9**, **10**, and **11** were obtained after repeated column chromatography. The entries 1 and 2 were similarly carried out by changing the solvent and the reaction temperature. The results are summarized in Table 1.

(Ethoxycarbonyl)(5-ethoxycarbonyltetrazol-2-yl)-α-(1,3-diphenyl-5-tetrazolio)methylide (9). Yellow crystals, Mp. 179–184°C (CH_2Cl_2/hexane); ir (KBr): 1744, 1680, 1552, 1490, 1380, 1362, 1346, 1238, 1224, 1186, 1118, 1072, 1040, 1022, 996, 898, 816, 758, 696, 682, 670/cm; ^{1}H NMR (200 MHz, deuteriochloroform): δ 3.58 (s, 3H, Me), 3.99 (s, 3H, Me), 7.30–7.41 (m, 5H, Ph), 7.61–7.68 (m, 3H, Ph), 8.19 (dd, 2H, J = 8.1 Hz, J = 1.7 Hz, Ph); ^{13}C NMR (50 MHz, deuteriochloroform): δ 50.6 (Me), 52.8 (Me), 78.7 (C^-), 120.7 (*o*-Ph), 124.8 (*o*-Ph), 129.1 (*m*-Ph), 129.9 (*m*-Ph), 130.6 (*p*-Ph), 132.6 (*p*-Ph), 133.2 (*i*-Ph), 135.1 (*i*-Ph); 156.5, 157.6, 158.0, 163.4 (CO_2Me × 2, C = N, C^+); uv/vis (MeCN): λ_{max} (log ε) = 392.0 (3.16), 279.0 nm (4.48). ms (EI, 70 eV): *m*/*z* 393 (32, M^++1-N_2), 293 (33), 248 (100), 231 (62), 219 (26), 169 (72), 131 (88), 119 (97), 101 (21). *Anal*. Calcd. for $C_{19}H_{16}N_8O_4$ (420.4): C, 54.28; H, 3.84; N, 26.66. Found C, 53.94; H, 3.76; N, 26.39.

Dimethyl 4-(4-phenylazophenylhydrazono)-4H-pyrazole-3,5-dicarboxylate (10). Orange crystals, Mp. 191–192.5°C (MeOH). ir (KBr): 2935, 2855, 1750, 1700, 1614, 1598, 1570, 1530, 1444, 1406, 1364, 1286, 1226, 1202, 1174, 1102, 1080, 1036, 844, 796, 770, 720, 684/cm. ^{1}H NMR (200 MHz, deuteriochloroform): δ 4.10 (s, 3H, Me), 4.15 (s, 3H, Me), 7.50–7.54 (m, 3H, Ph), 7.91–8.02 (m, 6H, Ph), 10.70 (bs, 1H, NH). ^{13}C NMR (50 MHz, deuteriochloroform): δ 53.7 (Me), 53.9 (Me), 121.8 (*o*-Ph), 122.8, 124.0 (Ph), 129.0 (*m*-Ph), 131.0 (*p*-Ph), 136.0 138.6 (*i*-Ph, C=N), 149.6, 152.0, 152.5, 155.5, 162.6, 165.7 (C—CO_2Me × 2, CO_2Me × 2, C—N=N—C); uv/vis (MeCN): λ_{max} (log ε) = 449.0 (3.36), 353.0 (4.53), 288.0 (4.07), 235.0 nm (4.22); ms (EI, 70 eV): *m*/*z* 393 (M^++1, 17), 392 (M^+, 69), 288 (19), 287 (100), 143 (10), 77 (56). *Anal*. Calcd. for $C_{19}H_{16}N_6O_4$ 0.5(CH_3OH) (408.4): C, 57.73; H, 4.04; N, 20.58. Found C, 57.36; H, 4.04; N, 20.65.

Dimethyl 4-(phenylhydrazono)-4H-pyrazole-3,5-dicarboxylate (11). Blass crystals; Mp. 159.5–162°C (MeOH); ir (KBr): 3280–2800, 1740, 1698, 1618, 1578, 1528, 1496, 1450, 1366, 1338, 1292, 1230, 1208, 1178, 1076, 1034, 962, 850–820, 772, 740, 730, 698/cm; ^{1}H NMR (200 MHz, deuteriochloroform): δ 4.07 (s, 3H, Me), 4.13 (s, 3H, Me), 7.20–7.27 (m, 1H, *p*-Ph), 7.40–7.48 (m, 2H, *m*-Ph), 7.77–7.81 (m, 2H *o*-Ph), 10.47 (bs, 1H, NH); ^{13}C NMR (50 MHz, deuteriochloroform): δ 53.5 (Me), 53.8 (Me), 121.6 (*o*-Ph), 125.7 (*p*-Ph), 129.2 (*m*-Ph), 135.8, 136.1 (*i*-Ph, C=N), 152.1, 155.6, 162.7, 165.7 (CO_2Me × 2, C—CO_2Me × 2); uv/vis (MeCN): λ_{max} (log ε) = 362.0 (3.44), 292.0 (4.21), 261 (3.96), 228 nm (3.97); ms (EI, 70 eV): *m*/*z* 289 (M^++1, 18), 288 (M^+, 100), 229 (41), 170 (77), 144 (82), 117 (72), 77 (73). *Anal*. Calcd. for $C_{13}H_{12}N_4O_4$ (288.3): C, 54.16; H, 4.20; N, 19.44. Found C, 54.00; H, 4.13; N, 19.01.

Reaction with tetracyanoethylene. DBU (0.15 mL, 1.0 mmol) was added to a mixture of **2b** (0.31 g, 1.0 mmol) and tetracyanoethylene (0.13 g, 1.0 mmol) in DMF (3.0 mL) at –60°C. The mixture was gradually warmed to room temperature and allowed to stand at room temperature for 3 h. Water was added and the black solid deposited was collected by filtration (0.33 g). The solid was chromatographed (SiO_2/CH_2Cl_2-MeCN gradient and MeOH) to give 12 (32 mg, 9%), 7 (59 mg, 25%), together with two unknown compounds. ^{1}H NMR and ^{13}C NMR spectra of the unknown compounds are very similar to those of 2. However, the structures of these products could not be determined.

(Cyano)(tricyanomethyl)-α-(1,3-diphenyl-5-tetrazolio)-methylide (12). Yellow crystals, Mp. 153–157°C (acetone/hexane); ir (KBr): 2940, 2180, 1592, 1560, 1486, 1466, 1456, 1364, 1342, 1292, 1268, 1176, 1072, 998, 842, 760, 720, 710, 688/cm; ^{1}H NMR (200 MHz, deuteriochloroform): δ 7.64–7.73 (m, 8H, Ph), 8.18 (dd, 2H, J_1 = 8.0 Hz, J_2 = 1.5 Hz, Ph). ^{13}C NMR (50 MHz, deuteriochloroform): δ 30.5 [—C(CN)$_3$], 38.6 (C^-), 107.4 (CN × 3), 115.9 (CN), 120.6 (*o*-Ph), 126.4 (*o*-Ph), 129.8 (*m*-Ph), 130.4 (*m*-Ph), 131.2 (*i*-Ph), 132.6 (*p*-Ph), 133.2 (*p*-Ph), 134.7 (*i*-Ph), 157.2 (C^+); uv/vis (MeCN): λ_{max} (log ε) = 379.0 (3.68), 276.0 nm (4.31); ms (EI, 70 eV): *m*/*z* 351 (M^++1, 3), 350 (M^+, 10), 324 (9), 270 (10), 245 (3), 194 (60), 179 (40), 152 (23), 128 (100), 118 (67), 103 (32). *Anal*. Calcd. for $C_{19}H_{10}N_8$ (350.35): C, 65.13; H, 2.88; N, 31.99. Found C, 64.94; H, 2.99; N, 32.18.

Reaction with *N*-phenylmaleimide. To a mixture of 2b (0.31 g, 1.0 mmol) and *N*-phenylmaleimide (0.17 g, 1.0 mmol) in DMF (3.0 mL) was added DBU (0.15 mL, 1.0 mmol) at –60°C, and the mixture was gradually warmed to room temperature in a period of 1.5 h, and then further stirred at room temperature for 1.5 h. Water was added and the products were extracted with dichloromethane. The extracts were dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue (0.32 g) was chromatographed (SiO_2/CH_2Cl_2:hexane =1:1 to MeOH) to give 13 (37 mg, 11%), 14 (22 mg, 9%), 15 (57 mg, 20%) and 7 (4 mg, 2%).

1,3,4-Triphenyl-1H-pyrrole-2,5-dione (13). Yellow crystals, Mp. 174–176°C (EtOH) (lit Mp. 175°C) [15].

1,3-Diphenyl-1H-pyrrole-2,5-dione (14). Pale yellow crystals, Mp. 115–120°C (EtOH) (lit Mp. 117°C) [16].

(2,5-Dioxo-1-phenylpyrrolidin-3-yl)phenylcyanamide (15). Colourless crystals; Mp. 138.5–140.5°C (acetone/hexane); ir (KBr): 2220, 1720, 1596, 1498, 1396, 1380, 1370, 1250, 1186, 748, 700, 684/cm; ^{1}H NMR (200 MHz, deuteriochloroform): δ 3.25 (dd, J = 18.4 Hz, J = 6.3 Hz, 1H, trans-CH_2), 3.46 (dd, J = 18.4 Hz, J = 9.1 Hz, 1H, cis-CH_2), 4.92 (dd, J=9.1 Hz, J = 6.3 Hz, 1H, CH), 7.21–7.55 (m, 10H, Ph); ^{13}C NMR (50 MHz, deuteriochloroform): δ 35.6 (CH_2), 59.1 (CH), 112.7 (CN), 120.0 (*o*-Ph), 127.4 (*p*-Ph), 127.9 (*o*-Ph), 130.8 (*p*-Ph), 130.9 (*m*-Ph), 131.7 (*m*-Ph), 132.6 (*i*-NPh), 140.9 (*i*-NCNPh), 172.9, 173.2 (C=O); ms (EI, 70 eV): *m*/*z* 292 (M^++1, 21), 291 (M^+, 100), 173 (63), 144 (90), 129, (17), 118 (56), 104

(70), 91 (65), 77 (81). *Anal*. Calcd. for $C_{17}H_{13}N_3O_2$ (291.304): C, 70.09; H, 4.50; N, 14.43. Found C, 70.12; H, 4.51; N, 14.47.

The reaction of 3-phenyl-1-*p*-tolyltetrazolium salt **2b′** and *N*-phenylmaleimide was similarly conducted as above to yield **13** (54 mg, 17%), **14** (26 mg, 10%), **15′** (70 mg, 23%), and **4′** (29 mg, 22%).

(2,5-Dioxo-1-phenylpyrrolidin-3-yl)-*p*-tolylcyanamide (15′). Colourless crystals, Mp. 140–142°C (acetone/hexane); ir (KBr): 3075, 2935, 2855, 2210, 1716, 1512, 1398, 1370, 1250, 1176, 818, 810, 740, 700/cm; ^{1}H NMR (200 MHz, deuteriochloroform): δ 2.36 (s, 3H, Me), 3.22 (dd, J = 18.5 Hz, J = 6.4 Hz, 1H, trans-CH_2), 3.43 (dd, J = 18.5 Hz, J = 9.2 Hz, 1H, cis-CH_2), 4.86 (dd, J = 9.2 Hz, J = 6.4 Hz, 1H, CH), 7.21–7.35 (m, 6H, Ph), 7.44–7.51 (m, 3H, Ph); ^{13}C NMR (50 MHz, deuteriochloroform): δ 20.7 (Me), 33.8 (CH_2), 57.9 (CH), 111.6 (CN), 118.9 (Ph), 126.2 (Ph), 129.0 (*p*-Ph), 129.2 (Ph), 130.5 (Ph), 130.9 (*i*-NPh), 135.9, 136.6 (*i*-NCNPh, *C*—Me), 171.3, 171.6 (C=O); ms (EI, 70 eV): *m*/*z* 306 (M^++1, 12), 305 (M^+, 55), 173 (100), 158 (42), 132 (9), 131 (90), 91 (78). *Anal*. Calcd. for $C_{18}H_{15}N_3O_2$ (305.33): C, 70.80; H, 4.95; N, 13.77. Found C, 70.46; H, 4.78; N, 13.64.

***p*-Tolylcyanamide (4′).** Oil; ir (KBr): 3175–2900, 2215, 1704, 1614, 1594, 1514, 1398, 1310, 1282, 1248, 804/cm; ^{1}H NMR (200 MHz, deuteriochloroform): δ 2.31 (s, 3H, Me), 6.31 (bs, 1H, NH), 6.91 (d, J = 8.5 Hz, 2H, Ph), 7.13 (d, J = 8.5 Hz, 2H, Ph) [17].

Reaction with fumaronitrile. To a mixture of **2b** (0.31 g, 1.0 mmol) and fumaronitrile (0.78 g, 1.0 mmol) in DMF (3.0 mL) was added DBU (0.15 mL, 1.0 mmol) at –60°C, and the mixture was gradually warmed to room temperature in a period of 1.5 h, and then further stirred at room temperature for 1.5 h. Water was added and the products were extracted with dichloromethane. The extracts were dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue (0.23 g) was chromatographed (SiO_2/CH_2Cl_2: hexane = 2:3→MeOH) to give **16** (21 mg, 9%), **17** (5 mg, 3%), **18** (11 mg, 7%) and **7** (18 mg, 8%). A mixture of **3** and **4** (42 mg, 3:4 = 31:69) was also obtained.

2,3-Diphenylfumalonitrile (16). Colourless crystals, Mp. 157–159°C (hexane) (lit Mp. 160–161°C) [18].

2-Phenylmaleonitrile (17). Colourless crystals, Mp. 37–43°C (lit Mp. 40.5–41°C) [18].

2-Phenylfumalonitrile (18). Colourless crystals, Mp. 86–91°C (hexane) (lit Mp. 87.5–88°C) [18].

Reaction with dimethyl acetylenedicarboxylate. To a mixture of **2b** (0.31 g, 1.0 mmol) and dimethyl acetylene-dicarboxylate (DMAD) (0.25 mL, 2.0 mmol) in DMF (2.0 mL) was added DBU (0.15 mL, 1.0 mmol) at –60°C, and the mixture was gradually warmed to room temperature in a period of 1.5 h, and then further stirred at room temperature for 1.5 h. Water was added and the products were extracted with dichloromethane. The extracts were dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue (0.57 g) was chromatographed (SiO_2/CH_2Cl_2-EtOAc gradient and MeOH) to give **19** (75 mg, 29% yield, *E*/*Z* mixture = 3:1) and **7** (18 mg, 8% yield). DMAD was recovered (53 mg, recovery 19%).

Dimethyl 2-(phenylcyanamido)-2-butenedicarboxylate (19). Pale yellow crystals; Mp. 77–85.5°C (CH_2Cl_2/hexane); ir (KBr, *E*/*Z* mixture): 2230, 1736, 1722, 1640, 1594, 1492, 1436, 1270, 1222, 1066, 1014, 894, 774, 760, 692/cm; ^{1}H NMR (200 MHz, deuteriochloroform, *E* isomer): δ 3.77 (s, 3H, Me), 3.81 (s, 3H, Me), 7.00 (s, 1H, =C*H*CO_2Me), 7.06–7.11 (m, 2H, *o*-Ph), 7.16–7.23 (m, 1H, *p*-Ph), 7.34–7.42 (m, 2H, *m*-Ph); ^{13}C NMR (50 MHz, $CDCl_3$, *E* isomer): δ 52.7 (Me), 53.6 (Me), 117.4 (*o*-Ph), 125.5, 126.1 (C=*C*HCO_2Me, *p*-Ph), 129.7 (*m*-Ph), 136.3, 139.0 (*C*=CH, *i*-Ph), 162.2 (*C*O_2Me), 162.5 (*C*O_2Me); uv/vis (MeCN, *E* isomer): λ_{max} (log ε) = 317.0 (3.37), 227 nm (4.23); ms (EI, 70 eV, *E*/*Z* mixture): *m*/*z* (%): 261 (M^++1, 18), 260 (M^+, 100), 245 (25), 229 (37), 201 (61), 200 (33), 169 (27), 157 (52), 142 (28), 115 (30). *Anal*. Calcd. for $C_{13}H_{12}N_2O_4$ (288.27): C, 59.99; H, 4.65; N, 10.77. Found C, 60.30; H, 4.70; N, 10.88.

Reaction of tetrazolium salt 2b with bis(1,5-cyclooctadiene)-μ,μ′-dichlorodirhodium (20). Typical procedure (Table 2, entry 1): A mixture of **2b** (0.16 g, 0.50 mmol) and bis(1,5-cyclooctadiene)-μ,μ′-dichlorodirhodium (**20**) (0.13 g, 0.25 mmol) in dry DMF (10 mL) was cooled to –60°C. DBU (75 μL, 0.5 mmol) was added and the mixture was stirred at −60°C for 3 h. Cold water was added and the precipitated solid (0.13 g) was filtered. The filtrate was extracted with CH_2Cl_2, washed with water, and dried (Na_2SO_4). The solvent was evaporated and the residue (90 mg) was chromatographed (SiO_2/CH_2Cl_2→ MeOH) to give bis(1,5-cyclooctadiene)-μ,μ′-dichlorodirhodium (16 mg, 12% recovery), **21** (29 mg, 12%), and **22** (16 mg). The precipitated solid was purified by column chromatography (SiO_2/CH_2Cl_2→MeOH) to give **22** (43 mg). The total yield of **22** is 59 mg (31%). Other reactions were conducted similarly, and the results are summarized in Table 2.

Complex 21. Yellow crystals, Mp. 165°C (EtOH); ir (KBr): 2940, 2860, 1488, 1362, 1230, 1140, 1014, 762, 680/cm; ^{1}H NMR (200 MHz, deuteriochloroform): δ 1.86–1.95 (m, 4H, cod-CH_2), 2.32–2.37 (m, 4H, cod-CH_2), 3.35 (s, 2H, cod-CH), 5.17 (s, 2H, cod-CH), 7.59–7.67 (m, 6H, Ph), 8.21–8.26 (m, 2H, Ph), 8.74–8.78 (m, 2H, Ph); ^{13}C NMR (50 MHz, deuteriochloroform): δ 29.0, 32.7 (cod-CH_2), 69.7 (d, J (^{103}Rh-^{13}C) = 14.3 Hz, cod-CH), 98.7 (d, J (^{103}Rh-^{13}C) = 7.2 Hz, cod-CH), 120.6, 123.9 (*o*-Ph), 128.9, 129.7 (*m*-Ph), 130.2, 131.6 (*p*-Ph), 135.0, 135.9 (*i*-Ph), 187.7 (d, J (^{103}Rh-^{13}C) = 51.6 Hz, Rh-C); uv/vis (MeCN): λ_{max} (log ε) = 280.5 (3.20), 384.0 nm (2.23). *Anal*. Calcd. for $C_{21}H_{22}ClN_4Rh$ (468.77): C 53.80, H 4.69, N 11.95; found C 53.70, H 4.60, N 11.90.

Complex 22. Yellow crystals, Mp. 152–154°C (EtOH); ir (KBr): 1590, 1492, 1468, 1358, 1310, 1230, 1124, 1096, 1038, 1010, 766, 684/cm; ^{1}H NMR (200 MHz, deuteriochloroform): δ 2.22–2.44 (m, 8H, cod-CH_2), 4.65 (s, 4H, cod-CH), 7.51–7.63 (m, 12H, Ph), 7.96–8.01 (m, 4H, Ph), 8.40–8.45 (m, 4H, Ph). ^{13}C NMR (50 MHz, deuteriochloroform): δ 31.1 (cod-CH_2), 90.7 (d, J (^{103}Rh-^{13}C) = 8.0 Hz, cod-CH), 120.6, 123.6 (*o*-Ph), 129.3, 129.9 (*m*-Ph), 130.8, 132.0 (*p*-Ph), 134.7, 135.2 (*i*-Ph), 185.3 (d, J (^{103}Rh-^{13}C) = 54.8 Hz, Rh-C); uv/vis (MeCN): λ_{max} (log ε) = 282.0 (3.37), 409.5 nm (2.21). *Anal*. Calcd. for $C_{34}H_{32}BF_4N_8Rh$ (742.01): C, 55.03; H, 4.31; N, 15.09. Found C, 54.86; H, 4.26; N, 14.96.

Reaction of tetrazolium salt 2b with complex 21. A mixture of **2b** (22 mg, 0.070 mmol) and **21** (33 mg, 0.070 mmol) in dry DMF (1 mL) was cooled to –60°C. DBU (11 μL, 0.07 mmol) was added and the mixture was stirred at –60°C for 4 h. Cold water was added and the precipitated solid (0.16 g) was filtered. The product was purified by column

chromatography (SiO_2/CH_2Cl_2) to give **22** (23 mg, 44%). A small amount of complex **21** was recovered (11 mg, 33%).

Reaction of ethynylbenzene and benzoyl chloride catalyzed by 21 or 22. A mixture of ethynylbenzene (0.33 mL, 3.0 mmol), benzoyl chloride (0.23 mL, 2.0 mmol), triphenylphosphine (5.2 mg, 0.020 mmol), and **21** (9.4 mg, 0.020 mmol) in octane (5 mL) was heated overnight at 140°C. 2-Methylnaphthalene (20 mg) was added as an internal standard, and the reaction mixture was analyzed by glc. The yield of the product (**23**) was estimated to be 61%. The mixture was chromatographed (SiO_2/hexane) and **23** was isolated (0.18 g, 43%). The reaction with **22** was similarly carried out and the yield of **23** was 22% (glc).

X-ray crystallography. X-ray analysis of **9** was performed on a sample recrystallized from CH_2Cl_2/hexane. Complex **21** was recrystallized from ethanol, and **22** from a mixture of CH_2Cl_2:EtOAc:hexane = 1:9:1.

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