Half-Sandwich Ruthenium(II) Complexes as Catalysts for Stereoselective Carbene−Carbene Coupling Reactions

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Received July 26, 1999

Cyclopentadienyl complexes of general formula [RuX(η^5-ligand)(PR_3)$_2$] have been found to catalyze the stereoselective decomposition of ethyl diazoacetate (EDA) to form diethyl maleate (DEM) in 95−99% purity with less than 1 mol % of catalyst, at temperatures depending on the bulkiness of the phosphine and the η^5-ligand as well as the nature of the anionic ligand X. A detailed study of the reaction between [RuCl(η^5-C_5H_5)(PPh_3)$_2$] and EDA suggests that dissociation of one PPh_3 is a key step of the catalytic process, which proceeds via the intermediate [RuCl(η^5-C_5H_5)(=$CHCO_2Et$)(PPh_3)]. Although this electrophilic carbene was not detected in the reaction mixture, it was independently prepared in solution at low temperature starting from [Ru(η^2-O_2CMe)(η^5-C_5H_5)(PPh_3). The acetate reacts with EDA at −40 °C to form the cyclic ester [Ru{$CH(CO_2Et)OC(Me)O$}(η^5-C_5H_5)(PPh_3), which on treatment with Me_2SiCl_2 gives the metal carbene postulated in the catalytic cycle. The stoichiometric reaction of the latter compound with EDA selectively affords the olefin derivative [RuCl(η^5-C_5H_5)(η^2-DEM)(PPh_3)], which was also detected in the catalytic cycle. The new complexes [RuCl(η^5-C_5H_5)(PR_3)$_2$] (PR_3 = PPh_2(2-MeC_6H_4), PPh_2Cy, P(3-MeC_6H_4)$_3$), bearing phosphines bulkier than PPh_3, have been prepared in high yield starting from ruthenium trichloride hydrate, cyclopentadiene, and phosphine in refluxing ethanol.

Introduction

α-Diazo carbonyl compounds have received increasing attention in recent years because of their manifold applications in organic synthesis via transition metal catalyzed reactions.[1] Coordinatively unsaturated complexes react with diazo compounds to generate transient electrophilic metal−carbenes,[2] which are key intermediates in carbon−carbon bond-forming processes of strategic importance, such as alkene cyclopropanation,[2a,3] olefin metathesis,[4] and carbon−hydrogen bond insertion.[2c,5] Furthermore, metal complexes decompose diazo compounds with formation of a mixture of cis and trans alkenes via carbene dimerization. Thus, ethyl diazoacetate (EDA) catalytically decomposes affording diethyl maleate (DEM, the kinetic product cis) and diethyl fumarate (DEF, the thermodynamic product trans), the DEM/DEF ratio depending on the catalyst employed. Highly stereoselective formation of DEM (93−96%) has been obtained with ruthenium[6,7] and osmium[8] porphyrin derivatives with overall yields above 90%. In comparison, Cu(II) salts,[9] $[Rh_2(OAc)_4]$,[10] and $[MCl_2(PPh_3)_3]$[11] (M = Ru or Os) catalyze EDA decomposition with lower DEM/DEF ratios.

Recently, we have found that the readily available complex [RuCl(η^5-C_5H_5)(PPh_3)$_2$] (**1a**) converts EDA into DEM quantitatively and with a purity higher than 99%, DEF being the only byproduct.[12] The DEM/DEF ratio obtained with **1a** is the highest reported to date. Likewise, complex **1a** catalyzes the decomposition of other N_2CHCOR compounds [R = Me, ^{n}Pr, ^{i}Pr and $(CH_2)_{10}CH_3$], affording quantitatively RCOCH=CHCOR carbene dimers, the cis isomer being formed in 95−97% yield.[12] Although reaction intermediates could not be isolated, the experimental data suggested a mechanism that implies formation of the carbene intermediate [RuCl(η^5-C_5H_5)(=$CHCO_2Et$)(PPh_3)], generated by the reaction between the α-diazo carbonyl compound and the 16-electron complex [RuCl(η^5-C_5H_5)(PPh_3)] (Scheme

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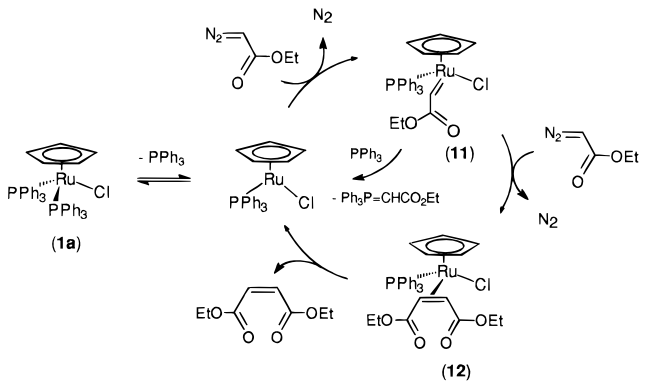
10.1021/om990582x CCC: $18.00
Publication on Web 11/06/1999

Scheme 1



1). The hypothesis of formation of a metal−carbene intermediate suggests that **1a**, and related half-sandwich ruthenium complexes, should display catalytic activity in a broad spectrum of processes involving carbene transfer reactions. The carbeneruthenium(II) species was not spectroscopically detected in the reaction mixtures, probably owing to its extremely low concentration in solution. However, preliminary results show that **1a** induces cyclopropanation of styrene from EDA as well as α-diazo carbonyl compound insertion into N−H and S−H bonds. All these reactions are believed to involve metal−carbene species.[1,2b]

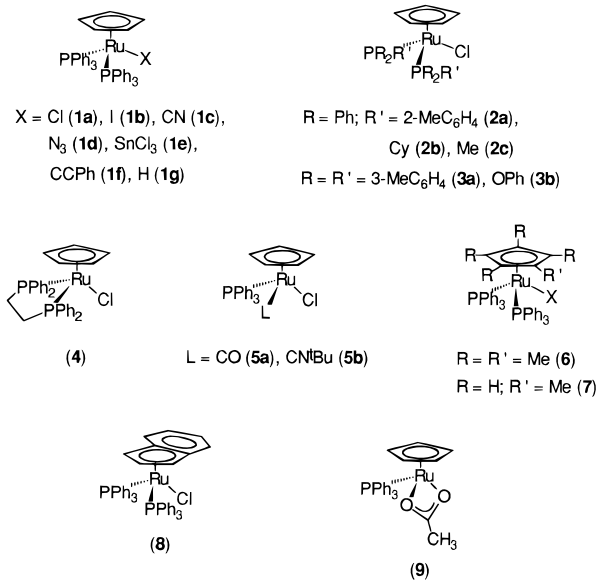
Half-sandwich cyclopentadienyl ruthenium complexes exhibit a rich and interesting chemistry, which is an area of current active research.[13] Although such complexes have been used in several stoichiometric and catalytic reactions,[14] hitherto their application in catalytic processes involving diazo derivatives has not been described.

As part of a program directed toward the investigation of the catalytic potential of this class of compounds, we have now tested several complexes related to **1a** in the decomposition of EDA, with the aim to understand the nature of the key steps occurring at the metal center. To obtain a better insight into the influence of both steric and electronic factors in the formation of the carbene intermediate, the complexes reported in Chart 1 have been employed. We also succeeded in the characterization in solution of [RuCl(η^5-C_5H_5)(=$CHCO_2$-Et)(PPh_3)] and [RuCl(η^5-C_5H_5)(η^2-DEM)(PPh_3)], previously proposed as intermediates in the catalytic decomposition of EDA (Scheme 1).[12] Moreover, the novel complexes [RuCl(η^5-C_5H_5)(PR_3)$_2$] (PR_3 = PPh_2(2-MeC_6H_4), **2a**; PPh_2Cy, **2b**; P(3-MeC_6H_4)$_3$, **3a**) have been synthesized and characterized.

Experimental Section

General Methods. All reactions were carried out under an argon atmosphere using standard Schlenck techniques. Solvents were carefully dried by conventional methods and distilled under argon before use. $RuCl_3$·*x*H_2O, P(3-MeC_6H_4)$_3$, N_2CHCO_2Et, Me_2SiCl_2, and diethyl maleate were purchased from Aldrich Chemical Co.; PPh_2Cy was purchased from Strem Chemical Co. The compounds [RuCl(η^5-C_5H_5)(PPh_3)$_2$] (**1a**),[15] [RuI(η^5-C_5H_5)(PPh_3)$_2$] (**1b**),[16] [Ru(CN)(η^5-C_5H_5)(PPh_3)$_2$] (**1c**),[17] [Ru(N_3)(η^5-C_5H_5)(PPh_3)$_2$] (**1d**),[18] [Ru($SnCl_3$)(η^5-C_5H_5)(PPh_3)$_2$] (**1e**),[19] [Ru(CCPh)(η^5-C_5H_5)(PPh_3)$_2$] (**1f**),[20] [RuH(η^5-C_5H_5)(PPh_3)$_2$] (**1g**),[16] [RuCl(η^5-C_5H_5)(PPh_2Me)$_2$] (**2c**),[21] [RuCl(η^5-C_5H_5){P(OPh)$_3$}$_2$] (**3b**),[22] [RuCl(η^5-C_5H_5)($PPh_2CH_2CH_2PPh_2$)] (**4**),[23] [RuCl(η^5-C_5H_5)(CO)(PPh_3)] (**5a**),[24] [RuCl(η^5-C_5H_5)(CN^tBu)(PPh_3)] (**5b**),[25] [RuCl(η^5-C_5H_4Me)(PPh_3)$_2$] (**6**),[26] [RuCl(η^5-C_5Me_5)(PPh_3)$_2$] (**7**),[21] [RuCl(η^5-C_9H_7)(PPh_3)$_2$] (**8**),[27] and [Ru(η^2-O_2CMe)(η^5-C_5H_5)(PPh_3)] (**9**)[28] were prepared according to the literature. NMR measurements were carried out using a Bruker AC 200 spectrometer. Chemical shifts, in ppm, are relative to TMS for ^1H and ^{13}C, and to 85% H_3PO_4 for ^{31}P. IR spectra were recorded with a Nicolet Magna 550 FT-IR spectrometer. Elemental analysis (C, H, N) were performed by the Microanalytical Laboratory of our department.

Chart 1



Synthesis of [RuCl(η^5-C_5H_5){PPh_2(2-MeC_6H_4)}$_2$] (2a). Ruthenium trichloride hydrate (400 mg, 1.53 mmol as $RuCl_3$·*x*H_2O) was dissolved in ethanol (10 mL) by bringing the mixture to a boil. After cooling, freshly distilled cyclopentadiene (1 mL, 12.1 mmol) was added. This solution was added dropwise to diphenyl-2-tolylphosphine (1.50 g, 5.43 mmol) dissolved in ethanol (40 mL) at the reflux point, and the

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suspension was stirred for 1 h. The yellow-orange product was filtered off, stirred in Et_2O for 4 h, and crystallized from dichloromethane/heptane. Yield: 890 mg (77%). Anal. Calcd for $C_{43}H_{39}ClP_2Ru$: C, 68.47; H, 5.21. Found: C, 68.31; H, 5.22. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 7.96 (q, 2H, ^3J(HH) = 4 Hz; aromatic protons), 7.32−6.96 (m, 26H; aromatic protons), 3.98 (s, 5H; C_5H_5), 1.70 (s, 6H; CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ = 142.2 (t, J(CP) = 2 Hz; *C*Me), 138.7 (pseudo t, J(CP) = 18.8 Hz; *ipso*-C_6H_4), 133.7 (t, J(CP) = 9.1 Hz; *m*-C_6H_4), 136.3 (*pseudo* t, J(CP) = 20.8 Hz; *ipso*-C_6H_5), 135.6 (pseudo t, J(CP) = 15.9 Hz; *ipso*-C_6H_5), 133.2 (t, J(CP) = 5.0 Hz; *o*-C_6H_5), 132.4 (t, J(CP) = 5.2 Hz; *o*-C_6H_5), 131.8 (t, J(CP) = 4.8 Hz; *o*-C_6H_4), 129.6 (s; *p*-C_6H_4), 128.5 (s; *p*-C_6H_5), 128.2 (s; *p*-C_6H_5), 127.6 (t, J(CP) = 4.5 Hz; *m*-C_6H_5), 127.3 (t, J(CP) = 4.2 Hz; *m*-C_6H_5), 124.6 (t, J(CP) = 5.8 Hz *m*-C_6H_4), 80.5 (t, J(CP) = 2.0 Hz; C_5H_5), 23.2 (t, J(CP) = 2.0 Hz; CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C): δ = 37.9.

Synthesis of [RuCl(η^5-C_5H_5)(PPh_2Cy)$_2$] (2b). The synthesis of **2b** was carried out as described for the corresponding complex **2a** by using PPh_2Cy in place of PPh_2(2-MeC_6H_4). Yield: 667 mg (59%). Anal. Calcd for $C_{41}H_{47}ClP_2Ru$: C, 66.70; H, 6.42. Found: C, 66.62; H, 6.35. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 7.38−7.15 (m, 20H; C_6H_5), 3.93 (s, 5H; C_5H_5), 2.62 (d, ^3J(H,H) = 11.6 Hz, 2H; Cy), 2.31 (pseudo t, ^3J(H,H) = 9.9 Hz, 2H; Cy) 1.75−0.85 (m, 18H; Cy). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): 138.5 (pseudo t, J(CP) = 16.6 Hz; *ipso*-C_6H_5), 136.7 (pseudo t, J(CP) = 18.5 Hz; *ipso*-C_6H_5), 133.8 (t, J(CP) = 4.9 Hz; *o*-C_6H_5), 132.5 (t, J(CP) = 4.2 Hz; *o*-C_6H_5), 128.7 (s; *p*-C_6H_5), 128.2 (s; *p*-C_6H_5), 127.7 (t, J(CP) = 3.9 Hz; *m*-C_6H_5), 127.1 (t, J(CP) = 4.5 Hz; *m*-C_6H_5), 80.3 (t, J(CP) = 2.3 Hz; C_5H_5), 39.8 (t, J(CP) = 9.1 Hz; *C*H), 28.7 (s; CH_2), 28.5 (s; CH_2), 27.6−27.1 (m; CH_2), 26.4 (s; CH_2). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C): δ = 38.7.

Synthesis of [RuCl(η^5-C_5H_5){P(3-MeC_6H_4)$_3$}$_2$] (3a). The synthesis of **3a** was carried out as described for the corresponding complex **2a** by using P(3-MeC_6H_4)$_3$ in place of PPh_2(2-MeC_6H_4). Yield: 682 mg (55%). Anal. Calcd for $C_{47}H_{47}ClP_2Ru$: C, 69.66; H, 5.85. Found: C, 69.39; H, 5.89. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 7.52−7.38 (m, 12H; C_6H_4), 7.30−7.23 (m, 12H; C_6H_4), 4.34 (s, 5H; C_5H_5), 2.39 (s, 18H; CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ = 138.5 (pseudo t, J(CP) = 20.1 Hz; *ipso*-C_6H_4), 136.6 (t, J(CP) = 4.9 Hz; *m*-C_6H_4), 134.3 (t, J(CP) = 5.2 Hz; *o*-C_6H_4), 131.0 (t, J(CP) = 4.9 Hz; *o*-C_6H_4), 129.4 (s; *p*-C_6H_4), 127.2 (t, J(CP) = 4.9 Hz; *m*-C_6H_4), 81.4 (t, J(CP) = 2.3 Hz; C_5H_5), 21.6 (CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C): δ = 39.1.

Spectroscopic Evidence of [Ru{CH(CO_2Et)OC(Me)O}(η^5-C_5H_5)(PPh_3)] (10). The complex Ru(η^2-O_2CMe)(η^5-C_5H_5)(PPh_3) (**9**) (21 mg, 0.043 mmol) was dissolved in 0.4 mL of toluene-d_8. The orange solution was cooled at −50 °C, and N_2CHCO_2Et (4.5 μL, 0.043 mmol) was added, affording a yellow solution after rapid nitrogen evolution. ^{1}H NMR (toluene-d_8, −40 °C): δ = 7.65−7.55 (m, 6H), 7.05−6.85 (m, 9H), 6.29 (d, 1H, ^3J(HP) = 15.6 Hz, PRuC*H*), 4.27 (s, 5H; C_5H_5), 4.24 (q, 2*H*, ^3J(H,H) = 7.3 Hz, CH_2CH$_3$), 1.20 (s, 3H; CH_3), 1.17 (t, 3H, ^3J(H,H) = 7.1 Hz, CH$_2$CH_3). ^{13}C{^{1}H} NMR (toluene-d_8, −40 °C): δ = 181.6 (*C*(O)OEt), 181.4 (d, ^3J(CP) = 2.8 Hz; O*C*(O)CH$_3$), 136.6 (d, ^1J(CP) = 36.2 Hz; *ipso*-C_6H_5), 134.2 (d, ^2J(CP) = 11.4 Hz; *o*-C_6H_5), 129.1 (*m*-C_6H_5), 128.0 (*p*-C_6H_5), 88.5 (d, ^2J(CP) = 11.4 Hz; Ru*C*H), 76.4 (d, ^2J(CP) = 2.9 Hz; C_5H_5), 58.5 (CH_2), 17.8 (CH_3CO), 15.1 (CH_3CH_2). ^{31}P{^{1}H} NMR (toluene-d_8, −40 °C): δ = 62.5.

Spectroscopic Evidence of [RuCl(η^5-C_5H_5){=CH(CO_2Et)}(PPh_3)] (11). Dichlorodimethylsilane (6.2 μL, 0.051 mmol) was added to the solution of complex **10** at −40 °C, prepared as described above. A change of color from yellow to green occurred slowly, and the spectra were recorded after 30 min. ^{1}H NMR (toluene-d_8, −40 °C): δ = 15.26 (d, ^3J(HP) = 16.9; Ru=C*H*), 7.7−6.8 (m, 15H), 5.11 (s, 5H; C_5H_5), 4.00 (q, 2H, ^3J(H,H) = 7.4 Hz, CH_2CH$_3$), 1.70 (s, 3H; CH_3), 0.97 (t, 3H, ^3J(H,H) = 7.2 Hz, CH$_2$CH_3). ^{13}C{^{1}H} NMR (toluene-d_8, −40 °C): δ = 274.3 (d, ^2J(CP) = 15.3 Hz; Ru=*C*H), 181.7 (CO), 137−128 (C arom), 94.9 (d, ^2J(CP) = 2.2 Hz; C_5H_5), 59.9 (CH_2), 14.4 (CH_3). ^{31}P{^{1}H} NMR (toluene-d_8, −40 °C): δ = 55.9.

Spectroscopic Evidence of [RuCl(η^5-C_5H_5)(η^2-DEM)(PPh_3)] (12). A red solution of [Ru(η^2-O_2CMe)(η^5-C_5H_5)(PPh_3)] (**9**) (19 mg, 0.0390 mmol) in 0.4 mL of benzene-d_6 was treated with diethyl maleate (DEM) (5.7 μL, d = 1.06 g/mL, 0.035 mmol). Dichlorodimethylsilane (4.5 μL, 0.037 mmol) was added to the yellow solution, and the NMR spectra were registered at room temperature. ^{1}H NMR (C_6D_6, 20 °C): δ = 7.70−6.80 (m, 15H; C_6H_5), 5.02 (s, 5H; C_5H_5), 4.20 (q, 2H, ^3J(HP) = 7.0 Hz, CH_2), 4.16 (d, H, ^3J(H,H) = 9.4 Hz; C*H*=CH), 3.98 (q, 2H, ^3J(HP) = 7.2 Hz, CH_2), 3.70 (dd, H, ^3J(H,H) = 9.4 Hz, ^3J(HP) = 14.0 Hz; CH=C*H*), 1.08 (t, 3H, ^3J(HP) = 7.0 Hz, CH_2), 0.96 (t, 3H, ^3J(HP) = 7.2 Hz, CH_2). ^{13}C{^{1}H} NMR (C_6D_6, 20 °C): δ = 170.2 (CO), 136−128 (aromatic C), 91.0 (d, ^2J(CP) = 2.6 Hz; C_5H_5), 60.8 (2CH_2), 57.6 (br, *C*H=CH), 50.7 (br, CH=*C*H), 14.6, (CH_3), 14.4 (CH_3). ^{31}P{1H} NMR (C_6D_6, 20 °C): δ = 49.6.

General Procedure for the Catalytic EDA Decomposition. The samples were typically prepared as follows: EDA (0.2 mmol) was added to 0.5 mL of benzene-d_6 containing the catalyst (2 μmol) under argon, and the solution was gently heated until nitrogen evolution started. After a few minutes the reaction was completed and the products were analyzed by NMR. No cyclopropanation products or other byproducts were detected in the reaction mixtures by NMR and GC−mass spectrometry.

Results and Discussion

Synthesis of Half-Sandwich Ruthenium(II) Complexes. The readily available complex **1a** has been employed as suitable starting product, because of its facility to give chloride or PPh_3 exchange reactions under relatively mild experimental conditions. However, attempts to obtain complexes from **1a** with phosphines bulkier than PPh_3, such as PPh_2Cy or P(3-MeC_6H_4)$_3$, resulted in the formation of only a very small amount of the corresponding mixed complexes [RuCl(η^5-C_5H_5)(PPh_3)(PR_3)]. Therefore, substitution of PPh_3 in **1a** seems to be strongly controlled by the steric properties of the incoming phosphine. Similarly the syntheses of **1a**, the half-sandwich complexes [RuCl(η^5-C_5H_5)(PPh_2R)$_2$] (R = 2-MeC_6H_4, **2a**; Cy, **2b**), and [RuCl(η^5-C_5H_5){P(3-MeC_6H_4)$_3$}$_2$] (**3a**) were obtained by addition of freshly distilled cyclopentadiene to a mixture of ruthenium trichloride hydrate and the corresponding phosphine in boiling ethanol. These compounds, bearing phosphines with cone angles larger than that of PPh_3 (145°), were isolated in high yield and characterized by NMR and elemental analysis. Their ^{1}H NMR spectra show the expected singlet for the η^5-coordinated C_5H_5 in the range δ 4.08−4.31, together with the appropriate resonances of phosphine protons, whereas the ^{31}P{^{1}H} NMR spectra exhibit a signal in the range δ 38−40. Characteristic ^{13}C{^{1}H} NMR signals are observed for the cyclopentadienyl carbon atoms at ca. δ 81. It should be noted that with phosphines having steric requirements higher than PPh_2(2-MeC_6H_4), such as PPh_2(2,6-Me$_2C_6H_3$), PPh_{3-n}(2-MeC_6H_4)$_n$ (n = 2, 3), and PCy_3, we were unable to isolate complexes of general formula [RuCl(η^5-C_5H_5)(PR_3)$_2$] by this route.

Ligands Effects in the Catalytic Decomposition of EDA. To explore the catalytic potential of complexes **1a**−**9** in the stereocontrolled carbene dimerization, their reactions with excess EDA in benzene-d_6 have been investigated.

Table 1. Temperatures of EDA Decomposition Induced by Half-Sandwich Ruthenium Complexes[a]

complex	T (°C)[b]
1e, 2c, 3b, 4, 5a, 5b	*c*
1c, 1d, 1f, 1g	>70
1a, 1b	65
3a	60
7	55
2b	50
8	45
6	35
9	20
2a	<20

[a] In benzene, 1 mol % catalyst. [b] Temperature at which dinitrogen evolution starts. [c] No EDA decomposition was observed even at 80 °C.

Complexes **1e**, **2c**, **3b**, **4**, **5a**, and **5b** are not catalytically active for EDA decomposition even at 80 °C. All other compounds decompose EDA with almost quantitative conversion into DEM and DEF, the former being present in the reaction mixture in yields higher than 95%. The best selectivity for the cis isomer (>99%) was however obtained with complex **1a**. Although the dimerization reaction takes place within a few seconds, as inferred by dinitrogen evolution, the temperature at which the decomposition reaction starts depends on the ruthenium complex employed (Table 1). Thus, for instance, complex **2a**, which contains the bulky ligand $PPh_2(2\text{-}MeC_6H_4)$, promotes evolution of N_2 below 20 °C, whereas even at 80 °C the derivative **2c** with the ligand PPh_2Me is catalytically nonactive. It is generally accepted that, in nonpolar solvents, one phosphine ligand in [RuCl(η^5-ligand)$(PR_3)_2$] complexes can be displaced at high temperature, affording a very reactive coordinatively unsaturated species [RuCl(η^5-ligand)(PR_3)].[21,24] The mechanism reported in Scheme 1 is in agreement with such a statement. Moreover, systematic studies on the reaction of **1a** with EDA have shown a strong inhibition of the reaction on addition of PPh_3, which implies that phosphine dissociation is most likely the rate-determining step. The lack of reactivity of complexes **3b**, **5a**, and **5b**, containing the low sterically demanding ligands $P(OPh)_3$, CO, and CNtBu, and **4**, bearing a chelate diphosphine, is probably due to a high activation barrier to ligand dissociation. In contrast, complex [Ru(η^2-O_2CH_3)(η^5-C_5H_5)(PPh_3)] (**9**), in which unsaturation can be achieved through a η^2 to η^1 conversion of the acetato ligand, is catalytically active even at 20 °C. The results collected in Table 1 suggest that the temperature of decomposition of EDA could be related to the lability of the phosphine ligand, namely, to the relative facility of formation of the 16-electron intermediate. In complexes [RuCl(η^5-C_5H_5)$(PR_3)_2$] the temperature at which EDA decomposition occurs decreases in the order PPh_2Me > PPh_3> $P(3\text{-}MeC_6H_4)_3$ > PPh_2Cy > $PPh_2(2\text{-}MeC_6H_4)$. This trend agrees with the results of Nolan and co-workers,[29] who suggest that the ruthenium−phosphorus bond in complexes of the type [RuCl(η^5-ligand)$(PR_3)_2$] weakens with the increase of phosphine cone angle.[30] As regards the influence of the η^5-ligand, the temperature at which nitrogen evolution starts decreases in the order η^5-C_5H_5 > η^5-C_5H_4Me > η^5-C_9H_7 > η^5-C_5Me_5. This is consistent with the kinetic studies performed by Gamasa and co-workers,[31] who have found that complex **8** dissociates PPh_3 an order of magnitude faster than **1a**, and also with the observation that isosteric phosphines are more strongly bound in the η^5-C_5H_5 compared to the η^5-C_5Me_5 system.[29b] It is likely that η^5-ligands in [RuCl(η^5-ligand)$(PPh_3)_2$], which can behave as an electron reservoir toward the metal fragment, favor the ruthenium−phosphorus bond cleavage and stabilize the 16-electron intermediate. Accordingly, indenyl and methylcyclopentadienyl have already been described as stronger donors with respect to cyclopentadienyl.[32]

Moreover, as evidenced by the data reported in Table 1, for complexes [RuX(η^5-C_5H_5)$(PPh_3)_2$] the temperature at which nitrogen evolution starts also depends on the nature of the ancillary ligand X. Apparently, when X has electron lone pairs, as Cl and I, the dissociation of one phosphine is favored, probably because the π-donor ability of the halide can stabilize the coordinatively unsaturated species.[33]

Mechanistic Studies. The decomposition reaction of EDA catalyzed by **1a** has been examined in detail, and the results agree with the mechanism depicted in Scheme 1. When a toluene solution of **1a** is treated at 65 °C with excess EDA (Ru:EDA ≈ 1:1000) a rapid evolution of N_2 occurs with quantitative formation of DEM and trace amounts of DEF. At room temperature no reaction is observed, and heating at 65 °C is necessary to start EDA decomposition. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture shows that during the catalytic reaction a new complex (δ 50.3) and the ylide $EtCO_2CH{=}PPh_3$ are formed in almost 1:1 molar ratio, along with trace amounts of the phosphazine $EtCO_2CHN_2{=}PPh_3$. The new ruthenium derivative was subsequently identified as [RuCl(η^5-C_5H_5)(η^2-DEM)(PPh_3)] (**12**) by comparison of the NMR data with those of an authentic sample prepared from [RuCl(η^5-C_5H_5){=CH-CO_2Et}(PPh_3)] (**11**) and EDA. The $^{31}P\{^1H\}$ NMR spectra recorded during the catalytic process show that the concentration of **1a** decreases by addition of subsequent amounts of EDA, with concomitant formation of **12** and $EtCO_2CH{=}PPh_3$. Removal of solvent and DEM from the final solution affords a dark brown mixture of **1a**, **12**, and $EtCO_2CH{=}PPh_3$, whose relative amounts depend on the number of catalytic runs performed. It is noteworthy that addition of PPh_3 to the reaction mixture converts promptly the labile complex **12** into **1a**. The phosphazine is formed in solution by an equilibrium reaction between EDA and the phosphine, without formation of the corresponding ylide even at 90 °C. For

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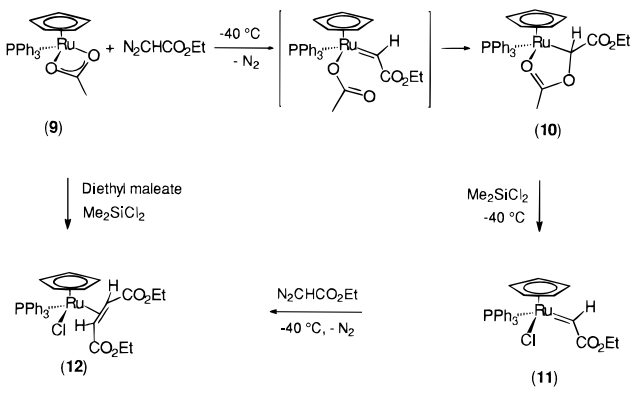
Scheme 2



the associative process log *K* values of about 2 and 1 at 20 and 80 °C, respectively, have been obtained by $^{31}P\{^1H\}$ NMR measurements in benzene-d_6. Catalytic runs (EDA/**1a** = 100) carried out in the presence of added PPh_3 show an increase of the temperature necessary to start the reaction. Thus, with equimolar PPh_3 and EDA, no evolution of N_2 was observed within 5 min at 65 °C. In the same conditions, at 80 °C no DEM was detected, but the solution contains PPh_3, phosphazine, and ylide in a 1:4:1.5 molar ratio. After 45 min the molar ratio changed to a 2:1:9, and DEM was also present in trace amounts, thus suggesting that PPh_3 is a better nucleophile for the carbene than EDA. All these experimental evidence are in agreement with the dissociative mechanism depicted in Scheme 1, which involves formation of the carbeneruthenium(II) complex **11**, which promptly reacts with EDA or PPh_3 to give DEM or $EtCO_2CH{=}PPh_3$, respectively. The presence of additional PPh_3 hinders the displacement of one phosphine from **1a** and the formation of the 16-electron complex [RuCl(η^5-C_5H_5)(PPh_3)]. Although detection of the highly reactive electrophilic carbene **11** in the reaction mixture failed, this compound was independently prepared and characterized in solution at low temperature, according to the procedure adopted by Werner and co-workers for the synthesis of the analogue [RuCl(η^5-C_5H_5)(=CPh_2)(PPh_3)].[34] When an equimolar amount of EDA was added to a toluene-d_8 solution of **9** at −50 °C, the orange solution turned yellow and N_2 evolution took place. However, the product formed was not the carbene [Ru(η^1-O_2CMe)(η^5-C_5H_5)(=$CHCO_2Et$)(PPh_3)], for which a $^{13}C\{^1H\}$ NMR signal at very low field (δ > 250) attributable to the Ru=C carbon atom is expected.[2d] Hence, a careful and complete analysis of both ^1H and $^{13}C\{^1H\}$ NMR spectra was carried out to identify the product, and all resonances have been unambiguously assigned. The most characteristic feature in the $^{13}C\{^1H\}$ NMR spectrum is the presence of a signal at δ 88.5 (^2J(PC) = 11.4 and ^1J(CH) = 154.4 Hz), which can be attributed to the carbon atom bound to ruthenium of the metallacyclo derivative [Ru{(CH(CO_2Et)OC(Me)O}(η^5-C_5H_5)(PPh_3)] (**10**) (Scheme 2). Furthermore, the ^1H NMR spectrum shows a doublet at δ 6.29 (J(PH) = 15.6 Hz), integrating for one proton, which is consistent with a C−H directly bound to ruthenium. It seems therefore conceivable that complex [Ru(η^1-O_2CMe)(η^5-C_5H_5)(=CH-CO_2Et)(PPh_3)] is indeed the initial product of the reaction between **9** and EDA, but subsequently a nucleophilic attack of the η^1-acetate group on the Ru=C bond yields the metallacycle **10.** Similarly, Werner has reported that **9** reacts with HC≡CCO_2Me to give, instead of the expected [Ru(η^1-O_2CMe)(η^5-C_5H_5)(=C=CRR′)(PPh_3)] complex,[28] a cyclic vinyl ester formed by a nucleophilic attack of the acetate carbonyl oxygen on the α carbon atom of the vinylidene intermediate. A similar cyclic ester has been obtained by reaction of sodium acetate with the carbene complex [RuCl(η^2-COPh)(=CH_2)(PPh_3)$_2$].[35]

Complex **10** is relatively stable in toluene-d_8 solution at temperatures below −30 °C, even in the presence of EDA, whereas at room temperature it slowly reacts with EDA to afford DEM. The conversion of **10** into the carbene complex **11** quickly occurs with chloride transfer agents via displacement of the acetato moiety. Thus, by addition of dicholorodimethylsilane to a toluene-d_8 solution of **10** at −40 °C, the color turns green and the signal at δ 62.5 in the $^{31}P\{^1H\}$ NMR spectrum disappears, whereas a new resonance appears at δ 55.9. The $^{13}C\{^1H\}$ NMR spectrum exhibits a doublet at δ 274.3 (J(PC) = 15.3 Hz) and the ^1H NMR spectrum shows a doublet at δ 15.26 (J(PH) = 16.9 Hz), which are consistent with the formation of a Ru=*CH*CO_2Et moiety.[36] These and the other features of both ^1H and $^{13}C\{^1H\}$ NMR spectra agree with structure **11**.

When an equimolar amount of EDA is added to a solution of **11** at −40 °C, nitrogen evolution occurs and the color turns yellow. The $^{31}P\{^1H\}$ NMR spectrum of the solution shows a single resonance at δ 50.2 at −40 °C in toluene-d_8, which can be attributed to the DEM derivative **12**. Thus, ruthenium carbene **11**, whereas stable for a few hours at low temperature, promptly undergoes a nucleophilic attack by EDA affording DEM. Compound **12** can also be obtained in solution from **9** by stepwise addition of DEM and Me_2SiCl_2 (Scheme 2). Hence, addition of an equimolar amount of DEM to **9** in benzene-d_6 at room temperature results in the formation of a yellow solution whose NMR features suggest the formation of the adduct [Ru(η^1-O_2CMe)(η^5-C_5H_5)(η^2-DEM)(PPh_3)] $^{31}P\{^1H\}$ NMR resonance at δ 49.7). Subsequent treatment with Me_2SiCl_2 affords a product whose $^{31}P\{^1H\}$ NMR spectrum exhibits the expected resonance at δ 50.2 attributed to **12**. The resonances of the olefinic protons are observed in the ^1H NMR spectrum as the AB part of an ABX spin system, where X is the ^{31}P nucleus, (δ H_A = 4.16, δ H_B = 3.70; $J(H_AH_B)$ = 9.4, $J(PH_B)$ = 14.0 Hz), as inferred by ^1H, ^1H-2D COSY, and ^{31}P-decoupled ^1H NMR measurements. In the $^{13}C\{^1H\}$ NMR spectrum the resonances of the olefinic carbon atoms appear at δ 57.6 and 50.7. These data can be compared to those of the related olefin−osmium complex [OsCl(η^5-C_5H_5)(η^2-DEM)(P^iPr_3)], isolated by Esteruelas and co-workers from [OsCl(η^5-C_5H_5)(P^iPr_3)$_2$] and EDA and characterized by NMR and X-ray analysis.[37] It should be noted that the

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direct interaction of **1a** with DEM in benzene-d_6 does not lead to displacement of PPh_3, even if an excess of olefin is used. By contrast, in the case of complex **2a** an equilibrium reaction takes place at room temperature with formation of the $PPh_2(2\text{-}MeC_6H_4)$ analogue of **12**.

Concluding Remarks

In summary, we have shown that a number of half-sandwich ruthenium(II) complexes of general formula $[RuX(\eta^5\text{-ligand})(PR_3)_2]$ are effective catalysts for the stereoselective decomposition of α-diazo carbonyl compounds to cis-olefins. The catalytic activity of the half-sandwich complexes depends on the formation of the coordinatively unsaturated $[RuX(\eta^5\text{-ligand})(PR_3)]$ species, which react with diazo compounds, affording metal-stabilized carbene intermediates. Apparently, the EDA decomposition starts at the temperature at which phosphine dissociation takes place, to form the catalytically active 16-electron complex. Bulky phosphines, electron-releasing η^5-ligands, and π-donor X favor reactions at lower temperature. The most characteristic feature of the decomposition reaction is the high selectivity for the cis-olefin, and this study has revealed that in half-sandwich ruthenium complexes the nature of the ancillary ligands has a minor influence on the stereoselectivity of the process. The origin of this stereoselectivity may be due to the steric influences of the ligands that force EDA to attack the electrophilic metal−carbene intermediate to give the less crowded cis π-olefin metal complex. Studies are currently in progress to scrutinize the catalytic potential of half-sandwich cyclopentadienyl- and pentamethylcyclopentadienylruthenium complexes in other reactions with diazo compounds, ranging from cyclopropanation and dipolar addition to insertion reactions.

Acknowledgment. This work was supported by the Italian Ministero dell'Università e della Ricerca Scientifica e Tecnologica (Rome). The authors thank Dr. P. Martinuzzi of the Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine, for assistance with the NMR measurements.

OM990582X

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