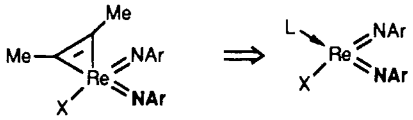
$$Re(NAr)_2X(py)_2 \xrightarrow[-2\text{ pyridine}]{+2\text{-butyne}} \underset{\mathbf{1b},\ \mathbf{2b}}{Re(NAr)_2X(2\text{-butyne})} \quad (4)$$

$$X = Cl\ (\mathbf{1b}),\ CH_2\text{-}t\text{-}Bu\ (\mathbf{2b})$$

ligands are equivalent and the ends of the coordinated 2-butyne are inequivalent, and in **2b** the methylene protons of the neopentyl ligand are equivalent. These data suggest that X, 2-butyne, and Re lie in the same plane, one that bisects the N–Re–N angle in the pseudotetrahedral species. This type of structure has been observed for the isoelectronic dioxo complexes $ReO_2(RC{\equiv}CR)R'$,[7] one of which has been structurally characterized,[7b] but the origin of the structure was not explained in this fashion.



X = Cl (**1b**), CH_2-*t*-Bu (**2b**)

Analogous reactions between **2a** and acetone, pivaldehyde, or norbornene (NBE) give yellow-brown $Re(NAr)_2(CH_2\text{-}t\text{-}Bu)(\eta^2\text{-}OCMe_2)$ (**2c**), $Re(NAr)_2(CH_2\text{-}t\text{-}Bu)(\eta^2\text{-}OCH\text{-}t\text{-}Bu)$ (**2d**), and $Re(NAr)_2(CH_2\text{-}t\text{-}Bu)(NBE)$ (**2e**), respectively. No ν_{CO} stretch is observed for **2c** or **2d** above 1450 cm^{-1}. NMR spectra again are consistent with a rigid pseudotetrahedral core geometry in which the π-bound ligand does not rotate about the ligand(centroid)–metal axis. Compounds **2c–e** are analogous to those recently reported for tungsten(IV) bis(imido) complexes having the $W(NAr)_2(PMe_2Ph)$ core instead of the $Re(NAr)_2X$ core;[3] the structure of $W(NAr)_2(PMe_2Ph)(\eta^2\text{-}OCMe_2)$ has been determined.[3]

$Re(NAr)_2(CH_2\text{-}t\text{-}Bu)Cl_2$ can be reduced in the presence of PMe_2Ph to give highly crystalline, diamagnetic $Re(NAr)_2(CH_2\text{-}t\text{-}Bu)(PMe_2Ph)$ (**2f**) in high yield. It is presumably a pseudotetrahedral relative of $W(NAr)_2(PMe_2Ph)_2$, and it reacts with 2-butyne to give **2b**.

All the above pseudotetrahedral bis(imido) complexes could be viewed as 18-electron complexes that contain four metal–imido π-bonds. The 16e $Re(NAr)_2X$ fragment, therefore, is isolobal and isoelectronic with MCp_2X (M = Nb, Ta; X = monoanionic ligand), if the imido ligands are counted as 6e dianionic $2\pi,1\sigma$-electron donors. We believe that $Re(NAr)_2X(py)_2$ species react with π ligands via loss of pyridine to give $Re(NAr)_2X(py)$, although associative processes cannot be ruled out at this stage.

Two NAr ligands contribute a significant amount of bulk to the coordination sphere. They are not as likely to bridge between metals as oxo ligands and thereby discourage potentially complicating bimolecular reactions. They also may discourage formation of six-coordinate bis(imido) complexes[8] and therefore maintain the system in the four-/five-coordinate manifold. Note that pseudotetrahedral bis(imido) complexes are related to imido alkylidene complexes containing bulky ligands such as $Mo(CH\text{-}t\text{-}Bu)(NAr)(OR)_2$,[9] which also react relatively readily (e.g., with olefins[10]) via five-coordinate intermediates.

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Supplementary Material Available: A description of synthetic procedures, NMR data, and analytical data (4 pages). Ordering information is given on any current masthead page.

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[7] (a) Felixberger, J. K.; Kuchler, J. G.; Herdtweck, E.; Paciello, R. A.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 946. (b) Cai, S.; Hoffman, D. personal communication.

[8] Preliminary studies (I.A.W.) suggest that $Re(NAr)_2Cl(py)_2$ reacts with $AgBF_4$ in methylene chloride in the presence of pyridine to give *trans*-$[Re(NAr)_2(py)_4][BF_4]$.

[9] Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

[10] Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158.

Transition-Metal-Substituted Diphosphenes. 22.[1] Cycloaddition Reactions of the Diphosphenyl Complex $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\text{–}P{=}P\text{–}Mes^*$ (Mes^* = 2,4,6-$tBu_3C_6H_2$) with Azodicarboxylates. X-ray Structure Analysis of $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\text{–}\overline{P({=}P\text{–}Mes^*)[N(CO_2Et)N{=}C(OEt)O}]$

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Summary: The diphosphenyl complex $(\eta^5\text{-}C_5Me_5)(CO)_2Fe{—}P{=}P{—}Mes^*$ (Mes^* = 2,4,6-$tBu_3C_6H_2$) undergoes a [1 + 4] cheletropic cycloaddition with the azodicarboxylates $RO_2C{—}N{=}N{—}CO_2R$ (R = Et, *t*Bu) to give the metal-substituted oxadiazaphospholenes $(\eta^5\text{-}C_5Me_5)(CO)_2Fe{—}\overline{P({=}P{—}Mes^*)[N(CO_2R)N{=}C(OR)O}]$ with exocyclic P=P bonds. The molecular structure of one of the compounds (R = Et) was elucidated by a single-crystal X-ray analysis.

Electron-releasing organometallic substituents considerably enhance the nucleophilicity of a diphosphene. In molecules such as $(\eta^5\text{-}C_5Me_5)(CO)_2M{—}P{=}P{—}Mes^*$ (Mes^* = 2,4,6-$tBu_3C_6H_2$; M = Fe, Ru, Os) the HOMO is mainly represented by the lone pair at the metalated phosphorus atom. This is documented by a number of reactions of $(\eta^5\text{-}C_5Me_5)(CO)_2Fe{—}P{=}P{—}Mes^*$ (**1**) with organic and organometallic electrophiles. The treatment of **1** with acrolein, methacrolein, and methyl vinyl ketone leads to oxaphospholenes I.[2]

With fumarodinitrile, maleodinitrile, dimethyl fumarate, and dimethyl maleate **1** generates all-trans-configurated

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[1] Part 21: Weber, L.; Frebel, M.; Müller, A.; Bögge, H. *Organometallics*, submitted for publication.

[2] Weber, L.; Frebel, M.; Boese, R. *Organometallics* **1989**, *8*, 1718.

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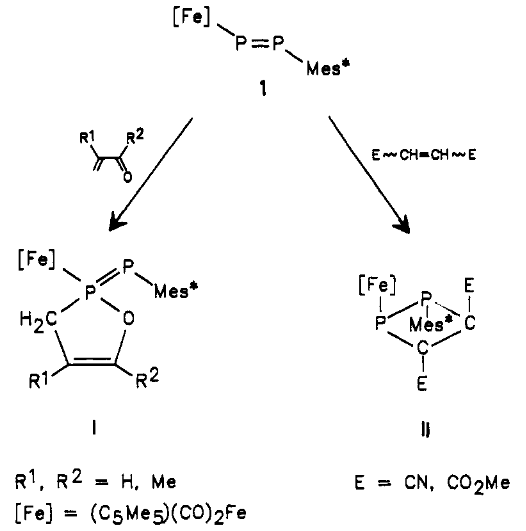
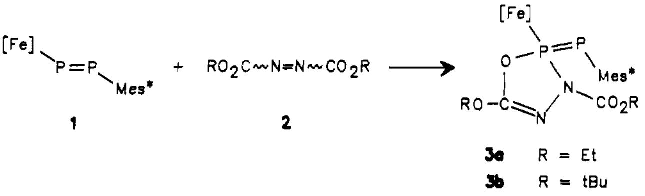


1,2-diphosphetanes.[3] Again, ring formation is presumably initiated by attack of the lone pair of the metalated P atom at the LUMO of the electrophile.

The step from electron-poor alkenes to azo compounds with electron-withdrawing substituents is obvious. Here we report on the chemical behavior of **1** toward diethyl azodicarboxylate (**2a**) and di-*tert*-butyl azodicarboxylate (**2b**), both of which are known as potent electrophiles.

Treatment of a THF solution of **1** with 1 equiv of the esters **2a,b** at −30 °C afforded the cycloadducts **3a,b** as red-brown crystalline solids.[4] The structure of **3** was assigned on the basis of spectral evidence[5] and confirmed by the single-crystal X-ray diffraction study of **3a**. The ^{31}P NMR spectra exhibit two doublets at δ 184.1 and −0.1 ppm (**3a**) and δ 180.5 and −7.75 ppm (**3b**), respectively. These shifts and the large coupling constants $^1J_{PP}$ (**3a**, 731 Hz; **3b**, 761 Hz) compare well with the ^{31}P NMR data of compound I ($R^1 = R^2 = H$) [δ(^{31}P) 162.2 (d), −28.2 (d) ppm; $^1J_{PP}$ = 727.5 Hz],[2] suggesting the presence of an ylidic PP bond within the molecule. Quartets at δ(^{1}H) 3.92 and 4.13 ppm as well as triplets at δ 1.01 and 1.11 ppm ($^3J_{HH}$ = 7.0 Hz) are caused by the chemically and magnetically different ethyl groups of **3a**. The *tert*-butyl groups of the ester functions of **3b** give rise to two singlets of equal intensity at δ(^{1}H) 1.51 and 1.52 ppm.



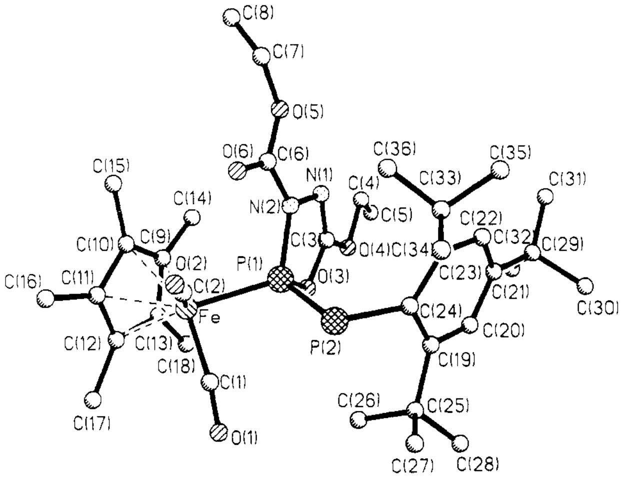


Figure 1. Molecular structure of **3a**.

Table I. Selected Bond Lengths (Å) and Angles (deg) for 3a

Bond Lengths

Fe–P(1)	2.241 (2)	Fe–C(1)	1.759 (9)
Fe–C(2)	1.778 (8)	P(1)–P(2)	2.074 (3)
P(1)–N(2)	1.744 (6)	P(1)–O(3)	1.709 (5)
P(2)–C(24)	1.870 (7)	N(1)–N(2)	1.422 (9)
N(1)–C(3)	1.266 (9)	N(2)–C(6)	1.367 (9)
O(1)–C(1)	1.147 (10)	O(2)–C(2)	1.142 (10)
O(3)–C(3)	1.349 (10)	O(4)–C(3)	1.322 (9)
O(4)–C(4)	1.443 (12)	O(5)–C(6)	1.325 (11)
O(5)–C(7)	1.449 (11)	O(6)–C(6)	1.213 (11)
Fe–Cp*	1.739 (8)		

Bond Angles

P(1)–Fe–C(1)	89.4 (3)	P(1)–Fe–C(2)	89.3 (3)
C(1)–Fe–C(2)	96.1 (4)	Fe–P(1)–P(2)	111.6 (1)
Fe–P(1)–N(2)	114.9 (2)	Fe–P(1)–O(3)	112.3 (2)
P(2)–P(1)–N(2)	118.1 (2)	P(2)–P(1)–O(3)	111.9 (2)
N(2)–P(1)–O(3)	85.3 (3)	N(2)–N(1)–C(3)	104.6 (6)
P(1)–P(2)–C(24)	101.1 (2)	P(1)–N(2)–N(1)	116.0 (4)
P(1)–O(3)–C(3)	111.6 (4)	Fe–C(1)–O(1)	171.5 (7)
N(1)–C(3)–O(3)	121.5 (7)	Fe–C(2)–O(2)	173.5 (7)
Cp*–Fe–C(1)	120.3 (4)	Cp*–Fe–P(1)	129.4 (4)
Cp*–Fe–C(2)	122.9 (4)		

In the ^{13}C{^{1}H} NMR spectrum of **3a** the terminal carbonyl ligands give rise to a multiplet at δ 213.2 and a singlet at δ 215.9. In **3b** these nuclei are observed as a multiplet at δ 213.7 and a doublet at δ 214.5 (J_{PC} = 24.8 Hz). Multiplets at δ 157.2 and 156.3 are assigned to the carbon atoms of the ester groups and the heterocycle in **3a** and **3b**, respectively.

In **4**, which is a compound containing similar oxadiazaphospholene cycles, the corresponding carbon atoms resonate at δ 153.2–154.1, whereas the ester carbonyl C atoms are found at δ 154.1–155.8.[4d]

Complex **3a** displays two intense ν(CO) bands for the $Fe(CO)_2$ groups at 2030 and 1985 cm^{-1} in the IR spectrum (pentane). In the cycloadducts of type I intense ν(CO) bands at lower wavenumbers are observed (ν 2018, 1966 cm^{-1}), which indicate the improved σ-donor/π-acceptor properties of the ring ligand of I in comparison to those of the P-heterocycle in **3**.

The most interesting feature of the molecular structure of **3a** (Figure 1 and Table I) is the geometry of the phos-

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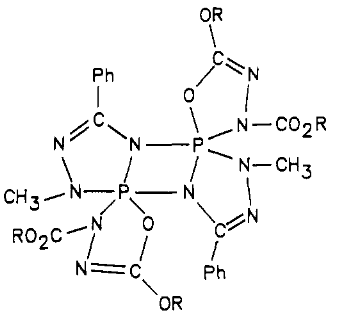
(3) Weber, L.; Frebel, M.; Boese, R. *Chem. Ber.* **1990**, *123*, 733.

(4) (a) Diazooxaphospholenes with five-coordinate phosphorus were previously obtained from phosphines and diethyl azodicarboxylate (see, e.g.: Majoral, J.-P.; Kraemer, R.; N'Gando M'Pondo, T.; Navech. J. *Tetrahedron Lett.* **1980**, *21*, 1307). (b) Goncalves, H.; Domroy, J. R.; Chapleur, Y.; Castro, B.; Faudeut, H.; Burgada, R. *Phosphorus Sulfur* **1980**, *147*. (c) A different route utilizes the cyclocondensation of trihalophosphoranes and acylhydrazines (see e.g.: Schmidpeter, A.; Luber, J.; Schomburg, D.; Sheldrick, W. S. *Chem. Ber.* **1976**, *109*, 3581). (d) There is one other example of the addition of azodicarboxylates to two-coordinate phosphorus: Tautz, H.; Schmidpeter, A. *Chem. Ber.* **1981**, *114*, 825.

(5) **3a**: ^{1}H NMR (300 MHz, C_6D_6) δ 1.01 (t, J = 7.0 Hz, CH_2CH_3), 1.11 (t, J = 7.0 Hz, CH_2CH_3), 1.43 (s, *p*-*t*Bu), 1.44 [s, $C_5(CH_3)_5$], 1.97 (s, *o*-*t*Bu), 3.92 (q, J = 7.0 Hz, CH_2CH_3), 4.13 (q, J = 7.0 Hz, CH_2CH_3), 7.45 (s, *m* aryl H); ^{13}C{^{1}H} NMR (75 MHz, THF-d_8): δ 9.43 [s, $C_5(CH_3)_5$], 14.38 (s, CH_2CH_3), 14.77 (s, CH_2CH_3), 31.77 [s, *p*-$C(CH_3)_3$], 33.91 [*o*-$C(CH_3)_3$], 35.66 [s, *p*-$C(CH_3)_3$], 39.19 [s, *o*-$C(CH_3)_3$], 61.22 (s, CH_2CH_3), 63.60 (s, CH_2CH_3), 97.09 [s, $C_5(CH_3)_5$], 123.80 (s, aryl C), 149.7 (s, aryl C), 153.02 (d, J = 3 Hz, *o* aryl C), 154.22 (d, J = 3 Hz, *o* aryl C), 157.15 [m, $C(O)O$], 213.20 [m, Fe(CO)], 215.91 [s, Fe(CO)]. **3b**: ^{1}H NMR (300 MHz, C_6D_6) δ 1.39 (s, *p*-*t*BuC), 1.50 [s, $C_5(CH_3)_5$], 1.51 (s, *t*BuO), 1.52 (s, *t*BuO), 1.97 (s, *o*-*t*BuC), 7.44 (s, *m* aryl H); ^{13}C{^{1}H} NMR (100 MHz, THF-d_8): δ 9.81 [s, $C_5(CH_3)_5$], 28.20 [s, $COC(CH_3)_3$], 28.71 (s, $COC(CH_3)_3$], 31.23 [s, $COC(CH_3)_3$], 31.80 [s, *p*-$C(CH_3)_3$], 33.95 (s, $COC(CH_3)_3$], 34.72 [s, *o*-C-$(CH_3)_3$], 34.98 [s, *p*-$C(CH_3)_3$], 39.46 (s, *o*-$C(CH_3)_3$], 98.54 [s, $C_5(CH_3)_5$], 120.55 (s, *m* aryl C), 134.38 (dd, J_{PC} = 76.5, 14.4 Hz, *i* aryl C), 146.95 (d, J_{PC} = 4.7 Hz, *p* aryl C), 152.57 (d, J_{PC} = 11.4 Hz, *o* aryl C), 154.35 (d, J_{PC} = 9.8 Hz, *o* aryl C), 156.33 [m, $C(O)O$], 213.65 (m, FeCO), 214.46 [d, J_{PC} = 24.8 Hz, Fe(CO)].



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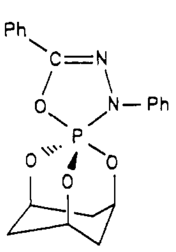
R = Me, Et, iPr, CH_2Ph



5

phorus-containing ligand, which is attached to the iron center by an Fe–P single bond of 2.241 (2) Å.[6] The exocyclic P–P bond distance [2.074 (3) Å] is comparable to the P–P bond [2.064 (2) Å] in I ($R^1 = R^2 = H$). The atoms Fe, P(1), P(2), and C(24) are no longer located in the same plane as is the case for educt **1** [torsion angle Fe–P(1)–P(2)–C(24) = 163.7°). The tetracoordinate phosphorus atom P(1) is part of a planar oxadiazaphospholene ring.

The bond lengths P(1)–N(2) [1.744 (6) Å] and P(1)–O(3) [1.709 (5) Å] are attributed to single bonds (calculated values are 1.76 and 1.72 Å, respectively).[7]

In I the P—O distance was determined to be 1.703 (5) Å. The endocyclic C=N bond [1.266 (9) Å] is close to the value of the C=N double bond in **5** [1.289 (7) Å].[8] The CO bond lengths C(3)–O(3) [1.349 (10) Å] and C(3)–O(4) [1.322 (9) Å] are significantly shorter than C(7)–O(5) [1.449 (11) Å] and C(4)–O(4) [1.443 (12) Å], which agrees with the π-conjugation of oxygen lone pairs to C(3).

Acknowledgment. Our work was generously supported by the Deutsche Forschungsgemeinschaft, Bonn, Germany, the Fonds der Chemischen Industrie, Frankfurt, Germany, and BASF AG, Ludwigshafen, Germany. This assistance is gratefully acknowledged.

Supplementary Material Available: Listings giving a structure determination summary, atomic positional parameters, bond lengths and angles, and anisotropic thermal parameters (8 pages); a table of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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(6) Crystal data for complex **3a**: space group $P\bar{1}$, $a = 9.863$ (3) Å, $b = 13.884$ (3) Å, $c = 14.484$ (4) Å, $\alpha = 82.72$ (2)°, $\beta = 84.85$ (3)°, $\gamma = 81.82$ (2)°, $V = 1942.2$ (10) Å^3, $Z = 2$, $\rho_{calcd} = 1.246$ g/cm^3, Mo Kα (graphite monochromator, $\lambda = 0.71073$ Å), ω scan data collection at room temperature ($4.0° \leq 2\theta \leq 48.0°$), 6064 unique reflections, 4134 unique observed reflections ($F > 4.0\sigma(F)$) Siemens R3m/V four-circle diffractometer, structure solved by direct methods and refinement by full-matrix least squares, with use of the Siemens SHELXTL PLUS software on a Micro VAX II computer. All non-hydrogen atoms were refined anisotropically with 424 parameters (hydrogen atoms in calculated positions riding on the corresponding C atoms; $U(H) = 0.08$ Å^2). $R = 0.093$, $R_w = 0.0795$, $w^{-1} = \sigma^2(F) + 0.0002F^2$, maximum rest electron density 0.5 e/Å^3.

(7) Holleman-Wiberg. *Lehrbuch der Anorganischen Chemie*, 81st–90th ed.; de Gruyter: Berlin, New York, 1976; p 129.

(8) Hamilton, W. C.; Ricci, S., Jr.; Ramirez, F.; Kramer, L.; Stern, P. *J. Am. Chem. Soc.* **1973**, *95*, 6335.

Organometallic Chemistry of Porphyrins: Spectroscopic and Chemical Characterization of a Rhodium Porphyrin–Ethyl Diazoacetate Adduct

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Summary: Iodorhodium(III) tetra-*p*-tolylporphyrin and ethyl diazoacetate (EDA) yield a 1:1 adduct possessing a metal–carbon bond. The ^{13}C and ^1H NMR spectra of this species suggest that it is a novel iodoalkyl complex resulting from formal insertion of the carbene fragment into the Rh–I bond. This and related species are of interest with regard to their potential roles in the rhodium porphyrin catalyzed cyclopropanation of alkenes by EDA.

Callot and co-workers have reported that Rh(III) porphyrins efficiently transfer carbene fragments derived from diazo esters to simple olefins.[1] These porphyrin-catalyzed cyclopropanations are unusual in a number of ways. They provide predominantly syn products when macrocycles with bulky substituents are employed, demonstrating that the carbene transfer step occurs within the porphyrin pocket and is not the result of the formation of free organic carbenes. More typical catalysts generally produce the anti isomer as the major product. In addition, the metal is in the 3+ oxidation state rather than the usual 2+ of common catalysts such as $Rh_2(OAc)_4$. We[2] and Callot[1] have also demonstrated that the porphyrin catalysts exhibit interesting substrate shape selectivity. For example, cis-disubstituted alkenes are somewhat more reactive than the trans isomers and tetrasubstituted alkenes are very poor substrates, allowing selective cyclopropanation of monosubstituted double bonds, a preference that may be useful synthetically. Finally, the small amount of work done in the area of porphyrin organometallic chemistry[3] has shown that the unique geometry and electronic properties of the macrocycle can lead to unusual reaction pathways.[4,5] Therefore, we have undertaken a mechanistic study of this reaction, including an analysis of the organometallic chemistry that ensues when EDA and rhodium porphyrins are allowed to react in the absence of alkene.

Iodorhodium tetra-*p*-tolylporphyrin (Rh(TTP)I; 0.1 mol %) efficiently catalyzes the reaction between styrene and ethyl diazoacetate (EDA) (10:1 molar ratio) at room temperature, providing a 98% yield (based on EDA) of the syn and anti cyclopropanes in 50 min. In order to address the chemical nature of the active intermediate in this system, we examined the stoichiometric reaction between Rh(TT-

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(1) Callot, H. J.; Metz, F.; Piechoki, C. *Tetrahedron* **1982**, 2365.

(2) Maxwell, J.; O'Malley, S.; Brown, K.; Kodadek, T. *J. Am. Chem. Soc.*, submitted for publication.

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(4) Paonessa, R. S.; Thomas, N. C.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *107*, 4333.

(5) Collman, J. P.; McElwee-White, L.; Brothers, P. J.; Rose, E. *J. Am. Chem. Soc.* **1986**, *108*, 1332.