



Supporting Information

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Approaching El Dorado: Discovery of Gold as Catalyst for Carbene Transfer Reactions from Ethyl Diazoacetate

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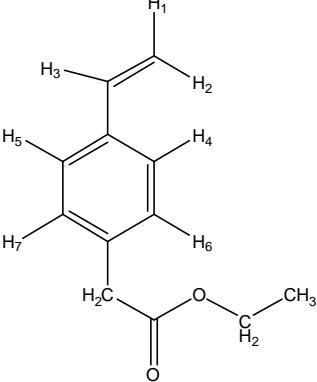
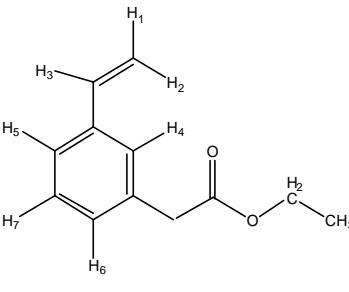
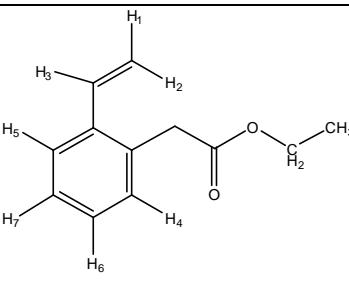
Catalytic reactions and product characterization.

1. Styrene.

Complex **2** (0.025 mmol) was dissolved in 1 mL of styrene and one equivalent of NaBAr₄’ was added to the solution. After 15 min of stirring, EDA (0.5 mmol) was added in one portion. After 1 h no EDA was detected in the reaction mixture. GCMS showed the formation of five compounds with the same molar mass. Two of them were identified as the *cis* and *trans* ethyl 2-phenylcyclopropane carboxylate. The other three species displayed identical mass spectra, that were assigned to phenylaceticacid, 4 ethenyl-, ethyl ester. The *para*- and *meta*- isomers have been reported in the literature.¹ However, for the sake of completeness, we have performed a detailed NMR study to characterize them, as shown in Table 1. In a similar experiment, 0.5 mmol of EDA were again reacted with 1 mL of styrene. After completion and removal of volatiles, trimethylvinylsilane was added as the internal standard to calculate, by ¹H NMR (CDCl₃) the mass balance (>98%) and the following ratio of products: *cis*-cyclopropane, 16%; *trans*-cyclopropane; 24 %; *o*-4 ethenylphenylaceticacid, ethyl ester, 12 %; *m*-4 ethenylphenylaceticacid, ethyl ester, 24% and *p*-4 ethenylphenylaceticacid, ethyl ester 24 %.

¹(a) *para*-isomer: Sing, N.; Krishan, K. *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya* 1974, 4, 908. (b) *meta*-isomer: Kasibhatla, S. R.; Bookser, B. C.; Probst, G.; Appleman, J. R.; Erion, M. D. *J. Med. Chem.* **2000**, 43, 1508.

**NMR and MS data for the three isomers of
phenylaceticacid, 4 ethenyl-, ethyl ester**

	¹ H NMR	¹³ C{ ¹ H} NMR	GCMS m/z
	H ₁ , 5.75, d (³ J = 17 Hz) H ₂ , 5.20, d (³ J = 10.5 Hz) H ₃ , 6.67, dd H ₄ , H ₅ , 7.10, d H ₆ , H ₇ , 7.38, d -CH ₂ CO ₂ , 3.72, s CO ₂ CH ₂ , 4.20, q -CH ₃ , 1.30, t	C ₆ H ₄ 125-130 =CH ₂ , 114.0 -CH=, 136.6 -CH ₂ -CO ₂ , 39.4 CO ₂ CH ₂ , 60.8 CH ₃ 14.5	190 (M) 177 (M-C ₂ H ₅) 162 (M-C ₂ H ₃) 117 (M-CO ₂ CH ₂ CH ₃) 102 (M-CH ₂ CO ₂ CH ₂ CH ₃)
	H ₁ , 5.34, d (³ J = 10.5 Hz) H ₂ , 5.62, d (³ J = 17 Hz) H ₃ , 6.98, dd H ₄ - H ₇ , 7.26-7.18 -CH ₂ CO ₂ , 3.63, s CO ₂ CH ₂ , 4.20, q -CH ₃ , 1.30, t	C ₆ H ₄ 125-130 =CH ₂ , 116.8 -CH=, 134.5 -CH ₂ -CO ₂ , 41.4 CO ₂ CH ₂ , 61.0 CH ₃ 14.2	190 (M) 177 (M-C ₂ H ₅) 162 (M-C ₂ H ₃) 117 (M-CO ₂ CH ₂ CH ₃) 102 (M-CH ₂ CO ₂ CH ₂ CH ₃)
	H ₁ , 5.77, d (³ J = 17 Hz) H ₂ , 5.26, d (³ J = 10.5 Hz) H ₃ , 6.65 dd H ₄ - H ₇ , 7.26-7.18 -CH ₂ CO ₂ , 3.60, s CO ₂ CH ₂ , 4.20, q -CH ₃ , 1.30, t	C ₆ H ₄ 125-130 =CH ₂ , 114.5 -CH=, 134.5 -CH ₂ -CO ₂ , 41.7 CO ₂ CH ₂ , 61.4 CH ₃ 14.4	190 (M) 177 (M-C ₂ H ₅) 162 (M-C ₂ H ₃) 117 (M-CO ₂ CH ₂ CH ₃) 102 (M-CH ₂ CO ₂ CH ₂ CH ₃)

2. Benzene.

Complex **2** (0.025 mmol) was dissolved in 3 mL of benzene and one equivalent of NaBAr₄’ was added to the solution. After 15 min of stirring, EDA (0.5 mmol) was added in one portion. Upon stirring for 6 h, no EDA was detected in the reaction mixture. The volatiles were removed and the residue dissolved in CDCl₃. NMR studies revealed the formation of two products: the cycloheptatriene formed via the Buchner reaction² and ethyl phenylacetate. The latter was identify by comparing the NMR and GCMS data with those of a commercial sample (ALDRICH). The mass balance was obtained by NMR using trimethylvinylsilane as the internal standard (added in the NMR tube at the end of the reaction). The ratio of products observed by NMR was 25% of cycloheptatriene and 75% of ethyl pheylacetate. No diethyl fumarate or maletae were observed.

3. Toluene.

Complex **2** (0.025 mmol) was dissolved in 3 mL of toluene and one equivalent of NaBAr₄’ was added to the solution. After 15 min of stirring, EDA (0.5 mmol) was added in one portion. Upon stirring for 3 h no EDA was detected in the reaction mixture. The volatiles were removed and the residue dissolved in CDCl₃. NMR studies revealed the formation of four products: the cycloheptatriene derivative and the *ortho*, *meta* and *para* isomers of ethyl tolylacetate. These three compounds were characterized by the direct comparison of their NMR and GCMS data with those of commercial samples (ALDRICH). The mass balance was assured by NMR using trimethylvinylsilane as internal standard. The ratio of products observed was: cycloheptatriene, 40%; ethyl o-tolylacetate, 27%; ethyl m-tolylacetate, 12%; ethyl p-tolylacetate 21%. No diethyl fumarate or maleate were observed.

² See: M. E. Morilla, M. M. Díaz-Requejo, T. R. Belderrain, M. C. Nicasio, S. Trofimenco and P. J. Pérez *Organometallics* **2004**, 23, 293 and referentes cited therein.

4. Cyclooctene.

Complex **2** (0.025 mmol) was dissolved in 1 mL of *cis*-cyclooctene and one equivalent of NaBAr₄' was added to the solution. After 15 min of stirring, EDA (0.5 mmol) was added in one portion. After 3 h no EDA was detected in the reaction mixture. GC studies revealed the exclusive formation of the *endo* and *exo* cyclopropanes.³ After removal of the volatiles, the residue was dissolved in CDCl₃ and styrene was added as internal standard to assess the mass balance based in EDA. No diethyl maleate nor fumarate was detected by GC or proton NMR. Endo:exo ratio, 25:75.

5. Amines.

Complex **2** (0.025 mmol) was dissolved in 3 mL of CH₂Cl₂ along with 20 equiv of the amine (aniline or *t*butyl amine) and one equivalent of NaBAr₄'. After 15 min stirring, EDA (0.5 mmol) was slowly added with the aid of a syringe pump for one hour, to avoid the insertion in both N-H bonds. NMR studies of the reaction crude in CDCl₃ revealed the complete conversion of EDA into the amine-insertion product, with no fumarate/maleate byproducts being observed. Styrene was used as internal standard to assess the quantitative (based in EDA) yields. Products were identified by NMR according to literature procedures.⁴

6. Alcohols.

Complex **2** (0.025 mmol) was dissolved in neat alcohol (3 mL) and one equivalent of NaBAr₄' was added to the solution. EDA (0.5 mmol) was added to the stirred solution in one portion. GC studies revealed the complete conversion of the alcohols into the corresponding ethers within 3 h. The yields and mass balance were established by GC using commercial samples (ALDRICH) of the products and styrene as internal standard (added at the end of the reaction). No diethyl fumarate or maleate were observed.

³ See: P. J. Pérez, M. Brookhart, J. L. Templeton. *Organometallics*, **1993**, *12*, 263 and references cited therein.

⁴ See: M. E. Morilla, M. M. Díaz-Requejo, T. R. Belderrain, M. C. Nicasio, S. Trofimenco and P. J. Pérez *Chem Commun* **2002**, 2998 and references cited therein.