Pergamon

Tetrahedron 54 (1998) 1639–1646

TETRAHEDRON

Palladium-Catalysed Coupling between Allyl Carbonates and Triethyl Methanetricarboxylate (TEMT)

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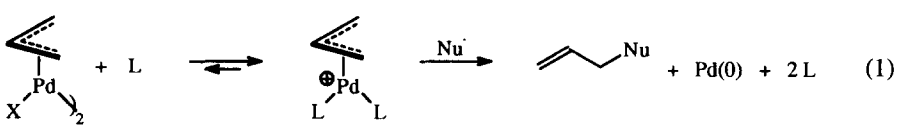
Received 8 October 1997; revised 17 November 1997; accepted 20 November 1997

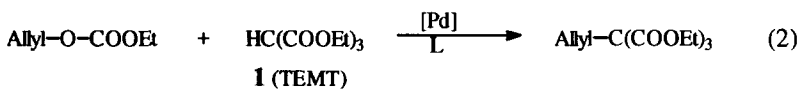
Abstract: Triethyl methanetricarboxylate (TEMT) is allylated by allylic carbonates in the presence of catalytic amounts of Pd(0) complexes; the reaction, conducted in very mild conditions, is fast and gives high yields of the title products.

(η^3-Allyl)palladium(0) complexes $[Pd_2(\mu\text{-}X)_2(\eta^3\text{-allyl})_2]$ **A** (also known as π-allyl Pd(0) complexes) are air-stable, easy-to-handle crystalline solids which are generally inert to a variety of reagents.[1] Their synthetic potential remained unexplored until Tsuji[2] observed that, in the presence of strongly coordinating solvents (*e.g.*, DMSO) or ligands (*e.g.*, phosphines), nucleophiles antifacially[3] attack the η^3-allyl ligand of the resulting cationic intermediate **B** leading to C-Nu bond formation (eq. 1).



Studies devoted to the synthetic utility of cationic η^3-allyl complexes have demonstrated that these intermediates undergo regio- and stereoselective S_N2 (or S_N2') nucleophilic substitution by a large and varied array of soft carbon and heteroatom nucleophiles. In this context Tsuji and Trost have reported impressive advances into Pd(0)-mediated allylic alkylation (Tsuji-Trost reaction, TTR) (Eq. 1), significantly expanding the domain of organopalladium chemistry.[4,5]

In connection with our interest[6] in the synthetic potential of triethyl methanetricarboxylate $HC(COOEt)_3$ (TEMT), we describe, herein, the utility of this reagent as a convenient *C*-nucleophile for Pd(0)-catalysed coupling with allylic carbonates, to afford the respective allylated compounds (Eq. 2).



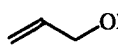
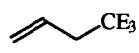
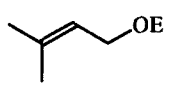
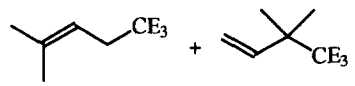
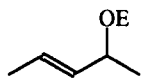
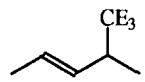
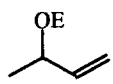
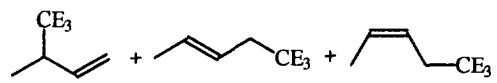
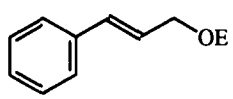
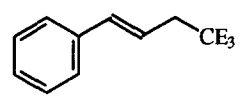
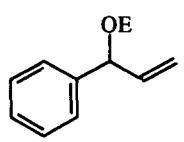
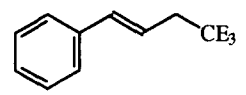
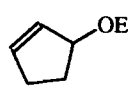
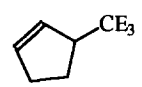
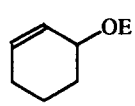
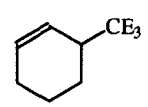
PII: S0040-4020(97)10371-4

TEMT has been shown to be a good surrogate for the malonate subunit, possessing significantly lower pK_{AH} (7.5 *vs* 13.3 for diethyl malonate) and precluding any diallylation. It is worthwhile mentioning that bis-allylated products often accompany reactions involving the addition of diprotic soft *C*-nucleophiles (*e.g.*, malonates) to (η^3-allyl)palladium complexes.[7] The resulting triesters were considered to have viable synthetic applications, since the $C(COOEt)_3$ moiety can be transformed into a wide variety of functionalities (*i,e,*, starburst dendrimers, two-carbon elongated carboxylic acids, α-alkylallyl alcohols, nitrogen containing heterocycles).[8]

Following reports from the Tsuji group,[9] we performed our initial experiments with allyl ethyl carbonate **2a** (readily prepared by reaction of allyl alcohol with ethyl chloroformate in pyridine at r.t.). As expected, the desired allylation of TEMT (Eq. 2) proceeded readily using a palladium catalyst in the presence of a phosphine as ancillary ligand. Thus, TEMT **1** (1.1 equiv.), tetrakis(triphenilphosphine)palladium(0) (2.5 mol %) and triphenylphosphine (TPP, 10 mol %) were sequentially added to **2a** (1.0 equiv.) at r.t. in dry CH_2Cl_2 under N_2. The immediate evolution of CO_2 occurred as the auxiliary ligand was added. The reaction was complete (GLC monitoring) within 5 minutes (!) after the addition of TPP, affording 79 % isolated yield of the allyl derivative **2b** (entry 1 - Table).

In order to optimize the reaction conditions, several combinations of Pd(0) catalysts and ancillary ligands were scrutinized. The best results in terms of Pd source were uniformly obtained with $Pd(PPh_3)_4$ and TPP in CH_2Cl_2 as solvent. Conversely, the use of $Pd_2(dba)_3{\cdot}CHCl_3$ - TPP led to sluggish and incomplete conversion, only partially overcome by the portionwise addition of TPP (up to 75 mol %). Moreover, dibenzalacetone (dba) released from the complex was difficult to remove from the reaction products due to the very close Rf similarity in the chromatographic conditions used for the purification step. It is of interest to note that the nature of the ancillary ligand did not appear to influence the course of the allylation since the reactions in the presence of $Pd(TPP)_4$ and different ligands (mainly phosphines)[10] all gave **2b** exclusively, with only minor differences in the yield values. Disappointingly, for unknown reasons, the use of 1,2-bis(diphenyl-phosphino)ethane (dppe) as auxiliary ligand in CH_2Cl_2 was found to decrease both the rate and the yield of the reaction.[11] The *in situ* generation of Pd(0)[12] species using a stable palladium source [*i.e.* $Pd(OAc)_2$, $Pd(acac)_2$] and TPP gave low yields as well as slow reactions: on the other hands, $PdCl_2(MeCN)_2$ and $PdCl_2(PhCN)_2$ led only to incomplete conversions, even in the presence of 100 mol% of TPP. The results reported here in CH_2Cl_2 changed little on varying the polarity of the solvent (*i.e.* DMF, THF or NMP). Under these optimized conditions [$Pd(TPP)_4$ (2.5 mol%), TPP (10 mol%), CH_2Cl_2, r.t.], the TTR applied to TEMT **1** (eq. 2) was effective with both primary and secondary allylic carbonates as well as with cyclic and acylic substrates. Tertiary allylic substrates were not examined in this study. After consumption of the carbonate (monitored by TLC or GLC), the reaction product(s) were isolated in fair to good yields by flash column chromatography. Results for a variety of structural types are presented in the Table, illustrating pertinent features of this protocol.

Table Tricarbethoxymethylation of allyl ethyl carbonates (E = CO_2Et) in the presence of $Pd(TPP)_4$-TPP[a]

Entry	Carbonate	Products (Yields, %)
1		
	2a	**2b** (79 %)
2		
	3a	**3b** (62 %) **3c** (20 %)
3		
	4a	**4b** (84%)[b]
4		
	5a	**5b** (21%) **5c** (54 %) **5d** (10 %)[c]
5		
	6a	**6,7b** (82 %)[b]
6		
	7a	**6,7b** (78 %)[b]
7		
	8a	**8b** (75 %)
8		
	9a	**9b** (81 %)

a) *Reaction conditions*: TEMT (1.2 mmol), carbonate (1.0 mmol), $Pd(TPP)_4$ (0.025 mmol), TPP (0.10 mmol) in dry (CaH_2) CH_2Cl_2 (10 ml) under N_2 at r.t.. b) (Z)-isomer <3% (GLC). c) Tentatively assigned by ^{1}H-NMR.

With regard to the regiochemical outcome of the allylic alkylation: this is controlled by i) the steric interaction between the incoming nucleophile and the allylic terminus, ii) the charge distribution of the π-allyl ligand on the metal and iii) the stability of the η^2-complex resulting from the alkene-metal complex as the initial product (association step, Scheme). Thus, with Pd complexes in the presence of donor ligands (*e.g.*, TPP), sterically demanding nucleophiles (such as the anion of TEMT **1**) react preferentially at the less substituted terminus of the η^3-allyl system.[13] Accordingly, with the sterically biased substrates **3a-7a** (entries 2-6), nucleophilic attack takes place at the less hindered terminus for all the unsymmetrical (η^3-allyl)palladium complexes, and the regiochemical outcome can be explained in terms of simple steric approach control arguments. Moreover, regioisomeric carbonates **6a** and **7a** produced exclusively the same (*E*)-product **6,7b** in similar yields, thereby indicating the intermediacy of a common and more thermodynamically stable *syn* η^3-allyl complex *en route* to **6,7b**.[14,15] The observed regioselectivity is most likely directed by the preservation of olefin-aromatic conjugation, whereas the lack of (*Z*)-product **6,7b** (arising from the less stable *anti* π-allyl complex) suggests that the dynamic π-σ-π equilibration[16] between the *syn* and *anti* complexes occurred at a faster rate than the nucleophilic attack.

In this study we have shown that the palladium catalysed allylation of TEMT proceeds very rapidly and cleanly under neutral conditions employing allylic carbonates as efficient precursors of the electrophilic (η^3-allyl)palladium species. Neither the nature of the ancillary ligand nor the polarity of the solvent appear to impact on product yields.

In view of the exceptionally mild conditions as well as the high yields, this protocol compares very favourably with published alkylation processes (*i.e.*, base-catalysed alkylation, Mitsunobu reaction). Furthermore, the tricarbethoxymethyl subunit of TEMT derivatives serves the function of a two- (or three-) carbon nucleophile equivalent and TEMT itself represents an useful addition to the list of nucleophiles that can be used in Pd-catalysed substitution.

EXPERIMENTAL

IR spectra (neat unless stated otherwise) were recorded on a Perkin Elmer 457 spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were measured in $CDCl_3$ with a Bruker AC 200 (200 MHz and 50.3 MHz, respectively). Mass spectra were obtained with a VG 7070 EQ spectrometer (CI-MS, isobutane). Analytical thin-layer chromatography was carried out on Merck Kieselgel 60 F254 (visualization with iodine or alkaline permanganate spraying). Methylene chloride and pyridine were both distilled under nitrogen from calcium hydride. Elemental combustion analyses were performed on Perkin Elmer 240 instrument and all new compounds gave satisfactory analyses (C ± 0.38%, H ± 0.30%). Gas-liquid cromatographic analyses were run on a Dani 86.10 gascromatograph equipped with a OV1 column (temperature program: 40°C, 1 min; 5°C/min → 120°C; 120°C, 40 min). All allylic alcohols are commercially available (Aldrich Chemical Co.) and are used without further purification. Cinnamyl alcohol was distilled before use. Cyclopenten-1-ol, cyclohexen-1-ol and 1-phenyl-3-propen-1-ol, were synthesized from the corresponding commercially available enones by

chemoselective reduction ($NaBH_4$, $CeCl_3$, MeOH, r.t.). Ethyl chloroformate, palladium(0) and palladium(II) complexes and the phosphine ligands are commercial products (Aldrich Chemical Co.), except for 1,2-bis(diphenyl-phosphino)benzene, purchased by Strem Chemicals, Inc.. All carbonates and products are colourless or slightly yellow oils.

Preparation of allylic carbonates: general procedure

In a round-bottomed three-necked flask, flame dried under nitrogen, is charged the allylic alcohol (1.0 mmol) dissolved in 5 ml of pyridine. The stirred solution is cooled to 0 °C and ethyl chloroformate (1.1 mmol) is slowly (5 min) added. The reaction mixture is stirred overnight, then poured into a beaker containing HCl 2M and crushed ice, and stirred until ice was completely dissolved. The mixture is extracted three times with methylene chloride. The organic extracts are washed with water, dried over sodium sulphate, filtered and evaporated using a rotary evaporator. The carbonate so obtained is sufficiently pure for the next step. Occasionally, more polar impurities are eliminated by filtration through a short column (5 cm) of silica gel, eluting with light petroleum-ethyl acetate (ratio depending from the substrate).

Allyl ethyl carbonate (2a) ^{1}H-NMR 5.95 ddt[1H] (J_1 = 17.2 Hz, J_2 = 10.0 Hz, J_3 = 5.7 Hz), 5.37 ddt[1H] (J_1 = 17.2 Hz, J_2 = 3.2 Hz; J_3 = 1.5 Hz), 5.27 ddt[1H] (J_1 = 10.3 Hz, J_2 = 2.7 Hz, J_3 = 1.4 Hz), 4.64 ddd[1H] (J_1 = 5.6 Hz, J_2 = 1.4 Hz, J_3 = 1.3 Hz), 4.22 q[2H] (J = 7.1 Hz), 1.36 t[3H] (J = 7.1 Hz); MS (CI) 131 (MH^+) - $C_6H_{10}O_3$ (130): calc.: C 55.37%, H 7.74 %; found: C 55.24%, H 7.78%.

Ethyl 3-methyl-2-butenyl carbonate (3a) ^{1}H-NMR 5.32 tqq[1H] (J_1 = 7.3 Hz, J_2 = J_3 = 1.4 Hz), 4.56 d[2H] (J = 7.2 Hz), 4.12 q[2H] (J = 7.1 Hz), 1.70 d[3H] (J =1.4 Hz), 1.66 d[3H] (J = 1.4 Hz), 1.23 t[3H] (J = 7.1 Hz); MS (CI) 159 (MH^+) - $C_8H_{14}O_3$ (158): calc.: C 60.74 %, H 8.92%; found 60.48%, H 9.01%.

Ethyl (3*E*)-3-penten-2-yl carbonate (4a) ^{1}H-NMR 5.76 dq[1H] (J_1 = 15.3 Hz, J_2 = 6.4 Hz), 5.48 ddq[1H] (J_1 = 15.3 Hz, J_2 = 7.0 Hz, J_3 = 1.7 Hz), 5.13 quint[1H] (J = 6.6 Hz), 4.16 q[2H] (J = 7.1 Hz), 1.68 dd[3H] (J_1 = 6.4 Hz, J_2 = 1.4 Hz), 1.33 d[3H] (J = 6.6 Hz), 1.28 t[3H] (J = 7.1 Hz); MS (CI) 159 (MH^+) - $C_8H_{14}O_3$ (158); calc.: C 60.74%, H 8.92%. found: 60.50%, H 8.88%.

3-Buten-2-yl ethyl carbonate (5a) ^{1}H-NMR 5.86 ddd[1H] (J_1 = 17.0 Hz, J_2 = 10.6 Hz, J_3 = 6.3 Hz), 5.19 m[3H], 4.18 q[2H] (J = 7.1 Hz), 1.36 d[3H] (J = 6.5 Hz), 1.30 t[3H] (J = 7.1Hz): MS (CI) 145 (MH^+) - $C_7H_{12}O_3$ - (144); calc.: C 58.32%, H 8.39%; found: C 58.46%, H 8.35%.

Cinnamyl ethyl carbonate (6a) ^{1}H-NMR 7.32 m[5H], 6.71 d[1H] (J = 15.9 Hz), 6.23 dt[1H] (J_1 = 15.8 Hz, J_2 = 6.3 Hz), 4.80 dd[1H] (J_1 = 6.3 Hz, J_2 = 1.1 Hz), 4.24 q[2H] (J = 7.1 Hz), 1.34 t[3H] (J = 7.1 Hz); MS (CI) 207 (MH^+) - $C_{12}H_{14}O_3$ - (206); calc.: C 69.88%, H 6.84%; found. 70.12%, H 6.85%.

Ethyl 1-phenyl-2-propenyl carbonate (7a) ^{1}H-NMR 7.37 m[5H], 6.10 m[1H], 6.03 dd[1H] (J_1 = 16.2 Hz, J_2 = 6.1 Hz), 5.34 m[2H], 4.19 q[2H] (J = 7.1 Hz), 1.32 t[3H] (J = 7.2 Hz); MS (CI) 207 (MH^+) - $C_{12}H_{14}O_3$ - (206); calc.: C 69.88%, H 6.84%; found. 70.01%, H 6.92%.

2-Cyclopentenyl ethyl carbonate (8a) ^{1}H-NMR 6.12 m[1H], 5.86 ddt[1H] (J_1 = 5.6 Hz, J_2 = 4.5 Hz, J_3 = 2.2 Hz), 5.60 m[1H], 4.16 q[2H] (J = 7.1 Hz), 2.53 m[1H], 2.30 m[2H], 1.95 m[1H], 1.28 t[3H] (J = 7.1 Hz); MS (CI) 157 (MH^+) - $C_8H_{12}O_3$ - (156); calc. C 61.52%, H 7.74%; found: C 61.29%, H 7.62%.

2-Cyclohexenyl ethyl carbonate (9a) ^{1}H-NMR 5.95 ddt[1H] (J_1 = 10.6 Hz, J_2 = 3.6 Hz, J_3 = 1.0 Hz), 5.75 ddt[1H] (J_1 = 10.6 Hz, J_2 = 3.8 Hz, J_3 = 1.9 Hz), 5.09 m[1H], 4.17 q[2H] (J = 7.1 Hz), 2.15-1.52 m[6H], 1.29 t[3H] (J = 7.1 Hz); MS (CI) 171 (MH^+) - $C_9H_{14}O_3$ (170); calc. C 63.51%, H 8.29%; found: C 63.50%, H 8.41%.

Palladium-catalyzed allylation: general procedure

In a round bottomed two-necked flask, flame dried under nitrogen, is poured the allylic carbonate (1.0 mmol) dissolved in 10 ml of dry methylene chloride. To this solution is added respectively TEMT **1** (1.1 mmol), $Pd(TPP)_4$ (0.025 mmol) and TPP (0.1 mmol). The yellow solution is stirred under nitrogen, and the reaction is monitored by TLC (light petroleum-ethyl acetate) or GLC. When the conversion is complete (5-30 min), the reaction mixture is evaporated to dryness; the residue is redissolved in diethyl ether and washed twice with 5% sodium hydroxide solution (to remove excess TEMT) and then with water. The organic phase is then dried over sodium sulphate, filtered and evaporated. Small amounts of triphenylphosphine are removed by filtration through a short (5 cm) column of silica gel the crude product dissolved in light petroleum and washing the column with petroleum ether. Further elution with petroleum ether-ethyl acetate split down the product, which is recovered by evaporation of the eluate.

Triethyl 3-Butene-1,1,1-tricarboxylate (2b) ^{1} H-NMR 5.99 ddt[1H] (J_1 = 17.1 Hz; J_2 = 10.0 Hz; J_3 = 7.1 Hz), 5.14 ddt[1H] (J_1 = 17.0 Hz; J_2 = 2.0 Hz; J_3 = 1.0 Hz), 5.10 ddt[1H] (J_1 = 10.0 Hz ; J_2 = 2.0 Hz; J_3 = 1.0 Hz), 4.28 q[6H] (J= 7.1 Hz), 2.87 ddd[2H] (J_1 = 7.1 Hz; J_2 = J_3 = 1.0 Hz), 1.27 t[9H] (J = 7.14 Hz); ^{13}C-NMR 166.5, 132.4, 119.1, 65.5, 62.0, 37.4, 13.8; MS (CI) 273 (MH^+) - $C_{13}H_{20}O_6$ - (272); calc. C 57.34%, H 7.40%; found: C 57.21%, H 7.41%.

Triethyl 3-Methyl-3-pentene-1,1,1-tricarboxylate (3b) ^{1}H-NMR 5.3 m [1H], 4.2 q[6H] (J = 7.2 Hz), 2.84 d[2H] (J = 7.7 Hz), 1.69 d[3H] (J = 7.7 Hz), 1.62 bs[3H], 1.27 t[9H] (J = 7.2 Hz).

Triethyl 2,2-Dimethyl-3-butene-1,1,1-tricarboxylate (3c) ^{1}H-NMR 6.40 dd[1H] (J_1 = 17.4 Hz, J_2 = 10.8 Hz), 5.07 dd[1H] (J_1 = 17.4 Hz, J_2 = 1.3 Hz), 5.04 dd[1H] (J_1 = 10.8 Hz, J_2 = 1.4 Hz), 4.23 q[6H] (J = 7.2 Hz), 1.40 s[6H], 1.28 t[9H] (J = 7.2 Hz).

Triethyl (3*E*)- 3-pentene-1,1,1-tricarboxylate (4b) ^{1}H-NMR 5.76 dq[1H] (J_1 = 15.3 Hz, J_2 = 6.4 Hz), 5.48 ddq[1H] (J_1 = 15.3 Hz, J_2 = 7.0 Hz, J_3 = 1.7 Hz), 5.13 quint[1H] (J = 6.6 Hz), 4.16 q[6H] (J = 7.1 Hz), 1.68 dd[3H] (J_1 = 6.4 Hz, J_2 = 1.4 Hz), 1.33 d[3H] (J = 6.3 Hz), 1.28 t[9H] (J = 7.1 Hz); ^{13}C-NMR 166.3, 131.0, 127.4, 69.2, 61.5, 40.9, 17.8, 17.0, 13.8; MS (CI) 301 (MH^+) - $C_{15}H_{24}O_6$ - (300); calc. C 59.98%, H 8.05%; found: C 60.11%, H 8.03%.

Triethyl 2-Methyl-3-butene-1,1,1-tricarboxylate (5b) ^{1}H-NMR 6.01 ddd[1H] (J_1 = 17.2 Hz; J_2 = 10.4 Hz ; J_3 = 2.6 Hz), 5.08 dd[1H] (J_1 = 17.2 Hz; J_2 = 1.9 Hz), 5.03 dd[1H] (J_1 = 10.2 Hz ; J_2 = 1.9 Hz), 4.22 q[6H] (J = 7.2 Hz), 3.15 m[1H], 1.24 t[9H] (J = 7.2 Hz), 1.21 d[3H] (J=7.0 Hz).

Triethyl (3*E*)-3-Pentene-1,1,1-tricarboxylate (5c) ^{1}H-NMR 5.61 dq[1H] (J_1 = 15.2 Hz, J_2 = 5.4 Hz), 5.49 dt[1H] (J_1 = 15.2 Hz, J_2 = 5.4 Hz), 4.22 q[6H] (J = 7.2 Hz), 2.78 d[2H] (J = 5.6 Hz), 1.62 d[3H] (J = 5.4 Hz), 1.24 t[9H] (J= 7.2 Hz).

Triethyl (3*Z*)-3-Pentene-1,1,1-tricarboxylate (5d) ^{1}H-NMR 5.55 m[2H], 4.22 q[6H] (J = 7.2 Hz), 2.87 t[2H] (J = 4.6 Hz), 1.62 d[3H] (J = 5.0 Hz), 1.24 t[9H] (J = 7.2 Hz).

Triethyl (3*E*)-3-Phenyl-3-butene-1,1,1-tricarboxylate (6,7b) ^{1} H-NMR 7.30 m[5H] , 6.49 d[1H] (J = 15.7 Hz), 6.39 dt[1H] (J_1 = 15.7 Hz ; J_2 = 6.2 Hz), 4.27 q[6H] (J = 7.1 Hz), 3.05 d[2H] (J = 6.2 Hz), 1.28 t[9H] (J = 7.1 Hz); ^{13}C-NMR 166.5, 137.0, 134.1, 128.3, 127.3, 126.2, 124.0, 65.9, 62.0, 36.8, 13.8; MS (CI) 349 (MH^+) - $C_{19}H_{24}O_6$ - (348); calc. C 65.50%, H 6.94%; found: C 65.29%, H 7.06%.

Triethyl 2-Cyclopentenylmethanetricarboxylate (8b) ^{1}H-NMR 5.81 m[2H], 4.24 q[6H] (J_1 = 7.2Hz), 3.69 m[1H], 2.35 m[2H], 2.17 m[1H], 1.8 m[1H], 1.27 t[9H] (J = 7.2 Hz); ^{13}C-NMR 166.6, 133.5, 130.2, 69.1, 61.7, 49.7, 31.8, 25.8, 13.8; MS (CI) 299 (MH^+) - $C_{15}H_{22}O_6$ - (298); calc. C 60.39%, H 7.43%; found: C 60.27%, H 7.51%.

Triethyl 2-Cyclohexenylmethanetricarboxylate (9b) ^{1}H-NMR 5.78 dt[1H] (J_1 = 10.5 Hz , J_2 = 2.7 Hz), 5.69 m[1H], 4.23 q[6H] (J = 7.1 Hz), 3.21 m[2H], 1.97 m[2H], 1.9-1.5 m[4H], 1.26 t[9H] (J = 7.1 Hz); ^{13}C-NMR 166.3, 129.8, 126.7, 68.4, 61.6, 40.0, 24.7, 24.6, 22.2 13.8; MS (CI) 313 (MH^+) - $C_{16}H_{24}O_6$ - (312); calc. C 61.52%, H 7.74%; found: C 61.58%, H 7.61%.

REFERENCES AND NOTES

1. a) Hegedus, L.S., "Transition Metals in the Synthesis of Complex Organic Compounds"; University Science Books: Mill Valley, CA, 1994; b) Maitlis, P.M.; Espinet, P.; Russell, M.J.C. "Allylic Complexes of Palladium(II)", in "Comprehensive Organometallic Chemistry"; Wilkinson, G., Ed; Vol. 6, pp. 385-446; Pergamon Press: Oxford, UK, 1982; c) Davies, J.A. "Palladium-Carbon π-Bonded Complexes", in "Comprehensive Organometallic Chemistry II"; Puddephatt, R.I., Ed.; Vol. 9, pp. 323-373; Pergamon: Oxford, UK, 1995; d) Harrington, P.J. "Transition Metal Complexes: Pd, W, Mo-Assisted Nucleophilic Attack", in "Comprehensive Organometallic Chemistry II"; Hegedus, L.S., ed; Vol. 12, pp. 797-904; Pergamon: Oxford, 1995.
2. a) Tsuji, J.; Takahashi, H.; Morikawa, M. *Tetrahedron Lett.* **1965**, 4387; b) Tsuji, J. *Bull. Chem. Soc. Jpn* **1973**, *46*, 1896; c) Trost, B.M.; Weber, L.; Strege, P.O.; Fullerton, T.J.; Dietsche, T.J. *J. Am. Chem. Soc.* **1978**, *100*, 3416.
3. Examples of *syn*-route for the oxidative addition of Pd(0) have been also reported (Starý, I.; Zajícek, J.; Kocovský, P. *Tetrahedron*, **1992**, *48*, 7229).

4. For recent reviews on Pd-catalysed allylic substitution reactions, see: a) Fiaud, J.C. in "Mechanisms in Stero-Differentiating Metal-Catalysed Reactions. Enantioselective Palladium Catalysed Allylation in Metal Promoted Selectivity in Organic Synthesis"; Graziani M.; Hubert, A.J., Noels, A.F., eds; Kluwer Academic Publishers: Dordrecht, 1991; p.107; b) Godleski, S.A. in "Comprehensive Organic Synthesis"; Trost, B.M., Ed; Pergamon Press: Oxford, 1991; p. 585; c) Frost, C.G.; Howarth, J.; Williams, J.M.J. *Tetrahedron: Asymmetry* **1992**, *3*, 1089; d) Hayashi, T. in "Catalytic Asymmetric Synthesis"; Ojima, I., Ed; VCH, 1993, p.325; e) Reiser, O. *Angew.Chem., Int. Ed. Engl.* **1993**, *32*, 547; f) "Palladium in Organic Synthesis", Tetrahedron Symposium-in-Print No. 52, Bäckvall, J.E., Ed *Tetrahedron* **1994**, *50*, 285; g) Heumann, A; Réglier, M. *Tetrahedron* **1995**, *51*, 975; h) Tsuji, J.; Mandai, T. *Angew.Chem., Int. Ed. Engl.* **1995**, *34*, 2589; i) Trost, B.M. *Acc. Chem. Res.* **1996**, *29*, 355; j) Trost, B.M.; Van Kranken, D.L. *Chem. Rev.* **1996**, *96*, 395; k) Williams, J.M.J. *Synlett* **1996**, 705; l) Heumann, A.; Réglier, M. *Tetrahedron* **1996**, *52*, 9289; m) Moreno-Mañas, M.; Pleixats, R. "Pd(II)-Catalysed Allylation of Heterocycles" in "Advances in Heterocyclic Chemistry", Vol. 66, Katritzky, A., Ed.; Academic Press: San Diego, CA, 1996, pp. 73-129; n) O'Donnell, J.M.; Chen, N.; Zhou, C.; Murray, A.; Kubiak, C.P.; Yang, F.; Stanley, G.G. *J. Org. Chem.* **1997**, *62*, 3962.

5. Copper, nickel, ruthenium, molybdenum, tungsten, platinum, rhodium, iridium and iron catalysts have also been reported to induce allylic substitution reactions. See, for example: a) Malkov, A.I., Baxendale, I.; Mansfield, D.J.; Kocovský, P. *Tetrahedron Lett.* **1997**, *38*, 4895; b) Takeuchi, R.; Kashio, M. *Angew.Chem., Int. Ed. Engl.* **1997**, 36, 263.

6. a) Cravotto, G.; Giovenzana, G.B.; Sisti, M.; Palmisano, G. *Tetrahedron* **1996**, *52*, 13007; b) Giovenzana, G.B.; Sisti, M.; Palmisano, G. *Tetrahedron: Asymmetry* **1997**, *8*, 515.

7. Foi, T.; Yanagisawa, A.; Miyazawa, M.; Yamamoto, K. *Tetrahedron: Asymmetry* **1995**, *6*, 389.

8. For a review on the chemistry of methanetricarboxylate esters: Newkome, G.R.; Baker, G.R. *Org.Prep. Proc.Int.* **1986**, *18*, 119.

9. Tsuji, J.; Minami, I. *Acc. Chem. Res.* **1987**, *20*, 140.

10. Commercially available ligands [*i.e.*, P(o-Tol)$_3$, , P(2-Furyl)$_3$, dppe, dppp, dppb, (Z)-$Ph_2PCH{=}CHPPh_2$, PCy_3, 1,2-bis(diphenylphosphino)benzene, $AsPh_3$ and $SbPh_3$] *in lieu* of TPP were also employed.

11. An example of this behaviour seen for a similar catalytic system has been found (Moreno-Mañas, M.; Pleixats, R.; Villaroya, M. *J. Org. Chem.* **1990**, *55*, 4925).

12. Amatore, C.; Jutand, A.; M'Barki, M.A. *Organometallics* **1992**, *11*, 3009.

13. See for example. Trost, B.M.; Verhoeven, T.R. *Compr. Organomet. Chem.* **1982**, *8*, 799.

14. For nomenclature of η^3-allyl complexes see: Consiglio, G.; Waymouth, R.M. *Chem. Rev.* **1989**, *89*, 257.

15. (η^3-Allyl)-Pd complexes tend to adopt a *syn* conformation while the less stable *anti* conformer is generally present in less than 10% (see: Öhler, E.; Kanzler, S. *Liebigs Ann.* **1997**, 1437).

16. Corradini, P.; Maglio, G.; Musco, A.; Paiaro, G. *Chem. Commun.* **1966**, 618.