Cationic Allylmetal Complexes. 9.[1] Dimerization Acrylates Catalyzed by Allylpalladium Complexes. Role of the Ligand and Indirect Evidence for the Occurrence of Hydridopalladium Species

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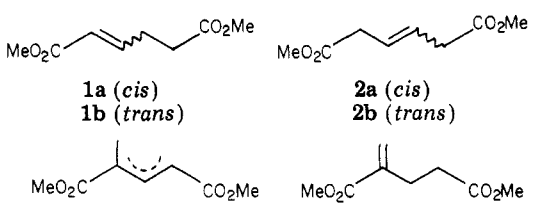
Summary: Selective dimerization of methyl acrylate to dimethyl *trans*-hex-2-enedioate is catalyzed by (η^3-allyl)(η^4-cycloocta-1,5-diene)palladium tetrafluoroborate in the presence of 1 equiv of basic phosphines. Model reactions suggest that a cationic hydridopalladium species, which is also active for double-bond isomerization, is formed prior to dimerization.

The catalytic dimerization of functional alkenes is an attractive route to bifunctional compounds. Among the products expected, the linear tail-to-tail dimers provide an alternative route to the manufacture of adipic derivatives from readily available feedstocks. In particular, the dimerization of methyl acrylate generally gives rise to a mixture of dimethyl hex-2-enedioates (**1a,b**), dimethyl



1a (*cis*) 1b (*trans*) 2a (*cis*) 2b (*trans*)

3 4

hex-3-enedioates (**2a,b**), dimethyl 2-methylpentenedioates (**3**), and dimethyl 2-methyleneglutarate (**4**). The latter compound is preferentially formed when tertiary phosphines[2] or [Co(salen)]$^-$[3] are used. The former dimers are generally built in the presence of transition-metal compounds like ruthenium and rhodium chlorides[4] and palladium dichloride.[5] Higher conversion of methyl acrylate is observed with the use of benzoquinone as a reoxidant of the reduced palladium.[6] Moreover, removal of chloride from $PdCl_2(PhCN)_2$[7] or $[(\eta^3\text{-}C_3H_5)PdCl]_2$[8] greatly increases the rate of the reaction. Therefore, cationic palladium complexes may act as precursors for that reaction as it has been already observed for other oligomerization reactions.[9,10] More recently, Nugent and his co-workers

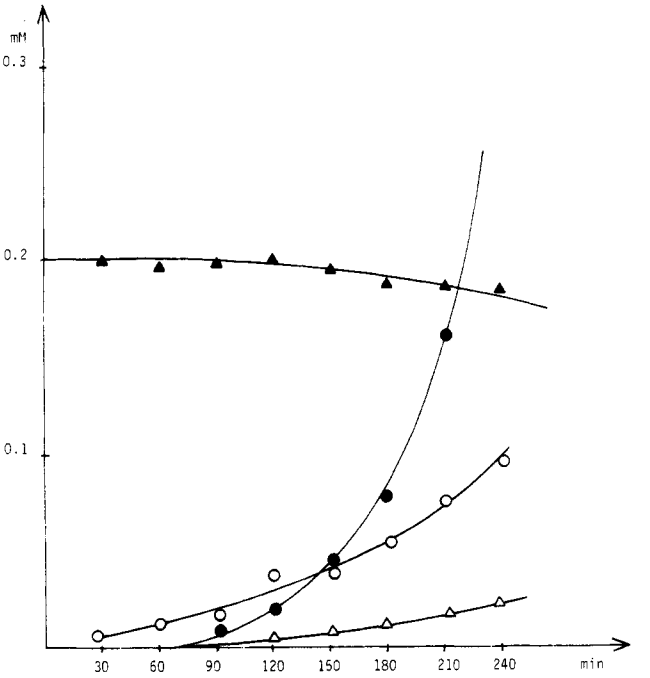
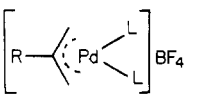


Figure 1. Primary products arising from the reaction of complex **5a** with excess of methyl acrylate in the presence of 1 equiv of PBu_3: ▲, 1,5-cyclooctadiene; △, 1,4- and 1,3-cyclooctadienes; ○, coupling product **7**; ●, dimer **1b**.

demonstrated the effect of Lewis and Brønsted acids on the rate enhancement of Pd-catalyzed methyl acrylate dimerization.[11] We wish to report that cationic allylpalladium complexes **5**,[12] provided they are modified with



5a, R = Me, L_2 = 1,5-cod
b, R = Me, L = PBu_3
c, R = Me, L = $MeNO_2$
d, R = Ph, L_2 = 1,5-cod

suitable phosphines, are able to catalyze this reaction and that hydridopalladium species are involved in the catalytic cycle. Table I shows that complex **5a** is inactive for acrylate dimerization even in the presence of benzonitrile or benzoquinone. Addition of P(III) ligands affords a catalyst for the dimerization of methyl acrylate. It can be seen from Table I that the nature of the phosphorus ligand and the P:Pd ratio strongly affect catalytic activity and product selectivity. The best results are observed for tributylphosphine and a P:Pd ratio of 0.5:1 to 1:1.[13] Noteworthy is the inhibition of the reaction for P:Pd ratio of 2 or more. In fact, complex **5b** is inactive for this reaction, a behavior similar to that reported for codimerization of 1,3-dienes and acrylates.[9b] However, the reaction occurs also with a 1:1 mixture of **5a** and **5b**. The main dimer obtained is dimethyl *trans*-hex-2-enedioate (**1b**)[14] when tributylphosphine was used. In this instance,

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(13) In blank experiments under the standard reaction conditions (80 °C, 20 h), PBu_3 slightly catalyzes the dimerization of methylacrylate to 4 (conversion ~2%): ^{1}H NMR ($CDCl_3$) δ 2.55 (2 H, d, J = 6 Hz), 2.57 (2 H, d, J = 6 Hz), 3.65 (3 H, s), 5.60 (1 H, s), 6.20 (1 H, s). Reactions with HBF_4 or $Pd_2(dba)_3{\cdot}HBF_4$ (1:1) led to polymers only.

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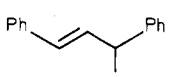
Table I. Dimerization of Methyl Acrylate with Complexes 5

cat. (mM)	additive(s) (mM)	P/Pd ratio	methyl acrylate, mM	reaction time, h	reaction temp, °C	methyl acrylate conversn, %	selectivities 1b	4	others
5a (0.2)			122	20	80	<1			
5a (0.2)	PhCN (0.2)		126	20	80	<1			
5a (0.2)	benzoquinone (1)		134	20	80	12	17		83
5a (0.2)	$LiBF_4$ (6.4)		139	20	80	<1			
5a (0.2)	PBu_3 (0.2)	1	140	20	80	48	89	2	8
5a (0.2)	PBu_3 (0.4)	2	127	20	80	<1			
5a (0.2)	PBu_3 (0.1)	0.5	126	20	80	58	92	1	7
5a (0.2)	PBu_3 (0.05)	0.25	122	20	80	9.5	85		15
5a (0.2)	PBu_3 (0.2)	1	137	5	80	23	82	2	16
5a (0.2)	PBu_3 (0.1)	0.5	128	5	80	27	96	1	3
5a (0.2)	PBu_3 (0.2)	1	134	67	80	50	92	2	6
5a (0.2)	PPh_3 (0.2)	1	129	20	80	11	74	4	22
5a (0.2)	$P(OPh)_3$ (0.2)	1	128	20	80	4.5	57		43
5a (0.1) + 5b (0.1)		1	135	20	80	25	90	2	8
5a (0.2)	PBu_3 (0.2) + benzoquinone (1)	1	127	20	80	20	70	0.5	29.5
5a (0.2)	PBu_3 (0.2) + $LiBF_4$ (6.4)	1	153	20	80	38	79	2	19

practically no change in selectivity is observed by varying the P:Pd ratio or the reaction time. Lower selectivities are observed for less basic phosphorus ligands. Finally, the addition of benzoquinone or excess of $LiBF_4$ to this system depresses the catalytic activity, therefore suggesting the occurrence of catalytic species and reaction mechanisms different from those recently reported.[10,11] The reaction has been examined for alkenes with other electron-withdrawing groups. Methyl methacrylate is slowly converted (12%) to a 63:37 mixture of two isomers;[15] vinyl acetate, acrylonitrile, and also methyl crotonate are unaffected by the **5a**–PBu_3 combination. Styrene is converted to **6**,[16] in



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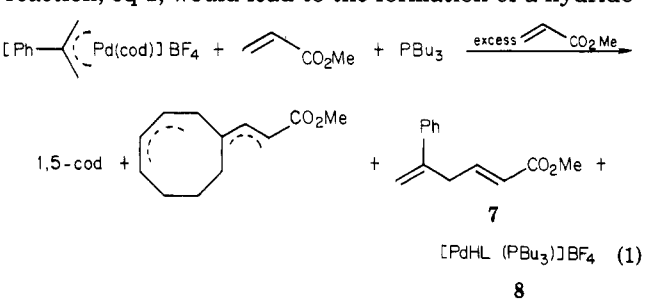
agreement with the observations reported for reaction with **5c**.[10] The mechanism of catalytic acrylate dimerization has been the subject of several proposals. Hydridopalladium,[4,5] vinylpalladium,[17] and palladium–carbene[18] intermediates have been discussed. Palladacyclopentanes can also be invoked on the basis of related work on iron[19] and of the thermal decomposition of palladacyclopentanes to (η^3-allyl)hydridopalladium species.[20] Under catalytic conditions, the reaction between a large amount of **5d** and methyl acrylate gives rise to the isolation in high yield of the adducts **7** between the alkene and the 2-phenylallyl ligand.[21] Isomers of the coupling product between 1,5-cyclooctadiene and methyl acrylate are also obtained. This reaction, eq 1, would lead to the formation of a hydrido-



7

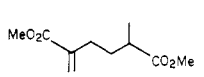
[PdHL (PBu_3)]BF_4 (1)

8

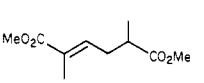
palladium species, **8**, which will be stabilized by tributylphosphine and potential ligands L (e.g., 1,5-cod, methyl acrylate, reaction products) available in the reaction mixture. Similarly, methyl 5-methyl-*trans*-hexa-2,5-dienoate (**9a**) has been characterized by GC/MS as a primary product during the catalytic methyl acrylate dimerization.[22] GC monitoring of the early stages of the reaction shows (i) the quantitative evolution of 1,5-cod after the addition of PBu_3, as already observed from ^1H NMR spectra,[9b] (ii) the formation of **9a**, and (iii) formation

(14) ^1H NMR ($CDCl_3$): δ 2.47 (4 H, d, J = 2 Hz), 3.67 (3 H, s), 3.72 (3 H, s), 5.85 (1 H, d, J = 16 Hz), 6.95 (1 H, ddt, J = 16, 6, 2 Hz). Dimethyl 2-methylene glutarate (**4**) has been also identified through GC and GC/MS comparisons with an authentic sample. Another dimer is formed in slight amounts and is tentatively assigned to **1a** since GC and GC/MS values do not fit with those of compounds **2** and **3**.

(15) Structures i (major isomer) and ii (minor isomer) are tentatively proposed on the basis of ^1H NMR and GC data of the mixture. In blank experiments, only polymerization is observed with HBF_4 or $Pd_2(dba)_3$·$CHCl_3$–HBF_4 (1:1).



i (63%)



ii (37%)

(16) **5a** (0.2 mM) is added to styrene (143 mM). Then PBu_3 (0.2 mM) is added and the mixture is heated at 80 °C for 2 h. The styrene conversion is 89%; selectivity for **6** is 90%. Practically the same results (respectively 93 and 91%) are observed in a run at 25 °C for 24 h. ^1H NMR($CDCl_3$): δ 1.48 (3 H, d, J = 7 Hz), 3.65 (1 H, ds, J = 7.3 Hz), 6.45 (2 H, d, J = 3 Hz), 7.33 (10 H, m). UV (2,2,4-trimethylpentane, c = 4.9 × 10^{-4} ML^{-1}): 250 (18 000), 284 (1600), and 293 (1000) nm, identical with that reported in: "DMS UV Atlas of Organic Compounds"; Butterworths-Verlag Chemie: London, 1966; Vol. 3.

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(21) PBu_3 (2.68 mM) is added to a solution of **5d** (2.68 mM) in methyl acrylate (10 mL). The solution is heated at 80 °C for 3 h. Separation on a column of silica gel affords **7** (1.73 mM, 65% based on **5d**) and isomers of **10** (1.88 mM, 70% based on **5d**). **7**: ^1H NMR ($CDCl_3$) δ 2.25 (3 H, s), 3.73 (3 H, s), 5.93 (1 H, d, J = 15 Hz), 6.53 (1 H, d, J = 12 Hz), 7.35 (5 H, m), 7.75 (1 H, dd, J = 12, 15 Hz); UV (2,2,4-trimethylpentane, c = 4 × 10^{-4} ML^{-1}) 302 (16 600) nm; IR (KBr, neat) 1720, 1620, 980, 765, 700 cm^{-1}.

(22) Methyl acrylate (30 mL) is added to a mixture of **5a** (1.99 mM) and **5b** (1.99 mM). The solution is heated at 80 °C for 50 min. After the distillation of the excess of methyl acrylate, the residue is purified on a column of silica gel. **9** is eluted with a cyclohexane–diethyl ether mixture (90:10): yield 1.5 mM (40% based on **5a** + **5b**); m/z 140; ^1H NMR ($CDCl_3$) δ 1.72 (3 H, s), 2.90 (2 H, d, J = 7 Hz), 3.72 (3 H, s), 4.80 (2 H, d, J = 6 Hz), 5.90 (1 H, d, J = 16 Hz), 7.00 (1 H, dt, J = 16, 7 Hz); IR (NaCl, neat) 1730, 1265, 1205, 1160, 980, 895 cm^{-1}. GC, ^1H NMR and IR patterns are different from those reported for the *cis* isomer **9b**.[23]

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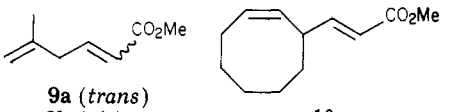

9a (*trans*)
9b (*cis*)

10

of **1b** *and* 1,4- and 1,3-cod (Figure 1).[24] Isomerization of **1b** to the thermodynamically less favored **2a,b** is not observed under the reaction conditions used. Noteworthy is the fact that the codimerization of a 1:1 (w/w) mixture of 1,5-cod and methyl acrylate gives rise to **10**, isomers of cod, and only trace amounts of **1b**.[25] The isomerization of 1,5-cod may proceed through reaction paths involving successive addition and elimination of **8** to one double bond of 1,5- and 1,4-cod. However, the mechanism of the palladium-catalyzed isomerization of olefins is still unclear since allylhydridopalladium[26] or cationic allylpalladium[27] species may also act as intermediates. Very few cationic hydridopalladium complexes have been isolated and characterized. They are stabilized by combinations of basic phosphines (e.g., $P(i\text{-}Pr)_3$) and chelating diphosphines (e.g., $Ph_2PCH_2CH_2PPh_2$).[28] Addition of the latter ligand during the course of the catalytic acrylate dimerization stops catalysis, but workup of the reaction mixture cannot afford a complex like **8** where $L_n = Ph_2PCH_2CH_2PPh_2$. Further studies directed toward the mechanism of this reaction that may be different from those of the reactions reported in the literature[7,10,11,27] are in progress.

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(24) **5a** (0.2 mM) and **5b** (0.2 mM) are dissolved in 1,2-dichloroethane (2 mL). *n*-Octane (internal standard) and methyl acrylate (2 mL) are added. Aliquots of this solution are placed in Carius tubes and heated to 60 ± 0.1 °C. Every 30 min one tube is cooled down, 2 equiv of PBu_3 are added in order to quench the catalyst, and the mixture is analyzed by GC. The results are reported in Figure 1.

(25) Methyl acrylate (11 mM) and cyclo-1,5-octadiene (8.6 mM) are added to a mixture of **5a** (0.2 mM) and **5b** (0.2 mM). The solution is heated at 80 °C for 31 h. Two fractions are collected from distillation: fraction 1 comprises 1,5-, 1,4-, and 1,3-cyclooctadienes (0.5 g, respectively 58, 7, and 35%); fraction 2 (0.78 g) corresponds to **10** [*m/z* 194; ^1H NMR ($CDCl_3$) δ 1.60 (8 H, br m), 2.15 (2 H, br m), 3.33 (1 H, m), 3.72 (3 H, s), 5.33 (1 H, dd, *J* = 11, 8 Hz), 5.72 (1 H, dt, *J* = 11, 7 Hz), 5.82 (1 H, d, *J* = 16 Hz), 7.00 (1 H, dd, *J* = 16, 7 Hz).

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A Twisted P–C Double Bond: Synthesis and Structure of a [(Methylene)phosphine]iron Tetracarbonyl Complex

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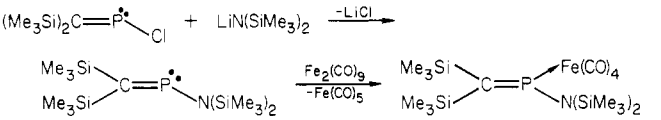
Summary: The reaction of $(Me_3Si)_2C{=}PCl$ with $LiN(SiMe_3)_2$ affords the tetrasilylated amino(methylene)phosphine **1** which reacts smoothly with $Fe_2(CO)_9$ yielding the η^1 complex $(Me_3Si)_2C{=}P[Fe(CO)_4]N(SiMe_3)_2$ (**2**). X-ray crystallographic analysis of **2** reveals an unusual coordination of the phosphine ligand in an equatorial position as well as a short (1.657 Å), but severely twisted (30.3°), P–C double bond.

The high level of current interest in unusually-hybridized phosphorus compounds has been stimulated, in part, by their potential as new types of ligands in organometallic chemistry. Among the (methylene)phosphines, $RP{=}CR_2$, for example, both σ (η^1) and π (η^2) complexes of the –P=C< moiety are now known.[1,2] With two exceptions,[2] however, all of the (methylene)phosphine complexes have contained the same ligand, $MesP{=}CPh_2$, first reported by Bickelhaupt.[3] In order to extend these studies to the use of other ligands, we have begun an investigation of the coordination chemistry of our recently prepared amino(methylene)phosphines.[4] We report here the synthesis of the new (methylene)phosphine $(Me_3Si)_2NP{=}C(SiMe_3)_2$ and its iron tetracarbonyl complex that is found to have an unusually twisted phosphorus–carbon double bond.

Treatment of lithium bis(trimethylsilyl)amide (68 mmol) in Et_2O (250 mL) at 0 °C with chloro[bis(trimethylsilyl)-methylene]phosphine[5] (68 mmol) afforded the tetrasilylated amino(methylene)phosphine **1** as a distillable yellow liquid [bp 61–63 °C (0.01 mm)] in 59% yield. A purified sample of **1** (ca. 5 mmol) was then allowed to react with 1 equiv of $Fe_2(CO)_9$ in pentane (25 mL) at room temperature with stirring for 18 h. Quantitative formation of the (phosphine)iron tetracarbonyl complex was shown by ^{31}P NMR spectroscopy, and **2** was isolated as dark orange crystals (mp 153–155 °C) by slow evaporation of the solvent. In addition to NMR spectroscopy (Table I), compounds **1** and **2** were characterized by satisfactory elemental analysis.[6]



1 **2**

Several aspects of the NMR spectra of **1** and **2** are structurally diagnostic. First, the low-field ^{31}P and ^{13}C chemical shifts in both compounds are indicative of sp^2 hybridization and strongly suggest η^1-coordination to $Fe(CO)_4$ via the phosphorus lone pair. Second, nonequivalence of the C-bonded Me_3Si groups due to hindered rotation about the P=C double bond is seen in the ^1H, ^{13}C, and ^{29}Si NMR spectra. Third, there is a substantial coupling ($^2J_{PC}$ = 18.6 Hz) between phosphorus and the carbonyl carbons of the $Fe(CO)_4$ group, indicating that **2** does not undergo the rapid intermolecular exchange of CO as observed for the analogous complexes of the isoelectronic aminophosphenium ions.[7]

(1) See, for example: (a) Klebach, Th. C.; Lourens, R.; Bickelhaupt, F.; Stam, C. H.; van Helrk, A. *J. Organomet. Chem.* **1981**, *210*, 211. (b) Kroto, H. W.; Nixon, J. F.; Taylor, M. J.; Frew, A. A.; Muir, K. W. *Polyhedron* **1982**, *1*, 89. (c) Al-Resayes, S.; Klein, S. I.; Kroto, H. W.; Meidine, M. F.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1983**, 930.

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(6) Compound **1**: Anal. Calcd for $C_{13}H_{36}NPSi_4$: C, 44.64; H, 10.37. Found: C, 44.37; H, 10.58. Compound **2**: Anal. Calcd for $C_{17}H_{36}FeNO_4PSi_4$: C, 39.45; H, 7.01. Found: C, 39.17; H, 7.00.

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