Diazadienes as control ligands in homogeneous catalysis

XVIII *. Palladacyclopentadienes and platinacyclopentadienes and the co-cyclotrimerization of various alkynes

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Abstract

Bis(dibenzylidene acetone)palladium reacts readily with N-aryl diazadienes (dad = ArN=CRCR=NAr) and two moles of dialkyl acetylenedicarboxylates EC≡CE (E = COOR) to form the palladacyclopentadienes (dad)$\overline{PdCE=CECE=CE}$ (2a–h). With a propiolic ester HC≡CE the corresponding complex (dad)$\overline{PdCH=CECE=CH}$ 3 is also formed in small yield. An η^2-alkyne complex 4 is obtained from the very bulky dad ^{t}BuN=CHCH=N^{t}Bu. The platinacyclopentadiene analogues of 2, (dad)$\overline{PtCE=CECE=CE}$ (5) have been prepared, but unlike the others are inactive in catalysis. The acetylenic diesters readily undergo cyclotrimerization with 2 as catalyst. Depending on the nature of the substituents, numerous alkynes R'C≡CR'' undergo a catalytic cyclo-cotrimerization with two moles of the diester EC≡CE to form a number of interestingly substituted benzenes. In the case of propargylic alcohols benzolactones are formed via a transesterification reaction during the catalysis. For phenylacetylene and EC≡CE not only the corresponding biphenyl derivative 8 but also the linear Z and E 1 : 2-addition products have been isolated.

Introduction

The cyclotrimerization of alkynes to form benzene derivatives is a thermodynamically favoured reaction, but a transition metal catalyst is normally required and numerous metals have been used, especially Ni^0 [1], Pd^0 [2] and Co^I [3]. Metallacyclopentadienes have been isolated as intermediates [4]. Before the reductive elimination of an aromatic compound a third alkyne molecule is probably coordi-

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* For part XVII and XVI see ref. 20.

nated to the metal and incorporated to form either a metallacycloheptatriene or, in a Diels–Alder-type reaction, a bicyclo[2.2.1]metallaheptadiene. The requirement of a vacant coordination site for the coordination of the third alkyne molecule is confirmed by the fact that closed-shell metallacyclopentadienes such as L_4Fe-CR=CRCR=CR [5] or L_2L_2'RuCR=CRCR=CR [6] do not react with alkynes even under drastic conditions.
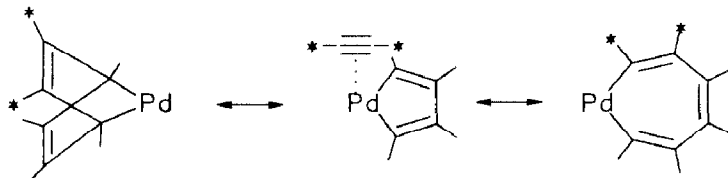

With nickel(0) and diazadienes (dad = RN=CR'CR'=NR) as additional ligands the mononuclear complexes (dad)Ni(η^2-alkyne) can be readily isolated [7]. They act as catalysts for the cyclotrimerization of alkynes [8]. With a number of monosubstituted alkynes, however, binuclear Ni–Ni bonded complexes (dad)Ni(μ-$C_4H_2R_2$)Ni(dad) were isolated [9], and are very good catalysts for the low-temperature cyclotetramerization of these alkynes to tetrasubstituted cyclooctatetraenes [10]. We were interested to see whether diazadienepalladium complexes would react with alkynes in the same way. We report here on the synthesis of palladium-alkyne complexes and their catalytic behaviour towards further alkynes.

Results and discussion

Synthesis of palladacyclopentadienes and an η^2-alkyne complex

By analogy with the synthesis of diazadienepalladium η^2-olefin complexes containing electron-poor olefins described by Vrieze et al. [11] bis(dibenzylideneacetone)palladium was treated with N-aryl diazadienes 1 and acetylenedicarboxylic acid esters at room temperature. A colour change from a dark violet to brown yellow was observed, and products 2 were isolated after evaporation of the solvent and were recrystallized from dichloromethane/diethylether.

(1)   (2)
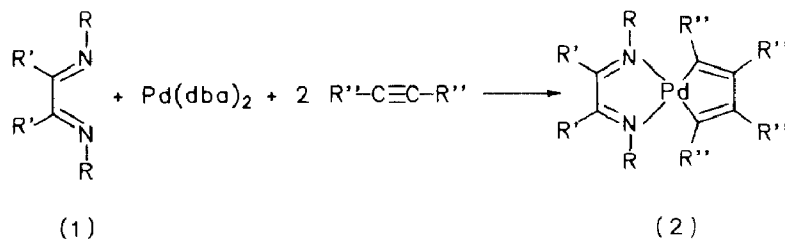
R		R'	R''
2a	2,6-Me$_2$C$_6$H$_3$	H	COOCH$_3$
b	2,6-Me$_2$C$_6$H$_3$	H	COOCH$_2$CH$_3$
c	2,6-(^{i}pr)$_2$C$_6$H$_3$	H	COOCH$_3$
d	4-MeC$_6$H$_4$	H	COOCH$_3$
e	4-MeOC$_6$H$_4$	H	COOCH$_2$CH$_3$
f	2,6-Me$_2$C$_6$H$_3$	Me	COOCH$_2$CH$_3$
g	2,6-Me$_2$C$_6$H$_3$	Me	COOCHMe$_2$
h	2,6-(^{i}pr)$_2$C$_6$H$_3$	Me	COOMe

(3)   (4)
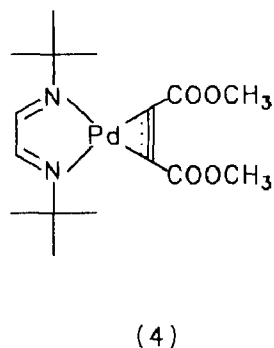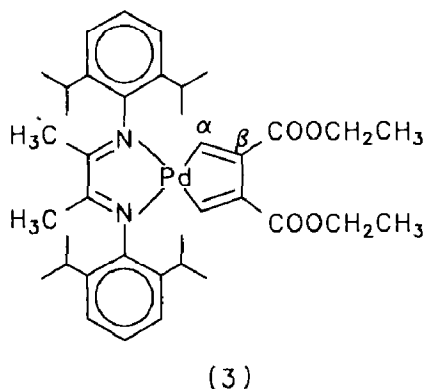
The direct synthesis of (dad)palladacyclopentadienes was unsuccessful with less activated alkynes such as propargylic alcohol, 2-butyne-1,4-diol and its dimethyl ether. With dad **1a** and propiolic acid ethyl ester the corresponding palladacyclopentadiene **3** was obtained in very low yield. In most cases use of N-alkyldiazadienes in this reaction was also unsuccessful. In the case of the very bulky N,N'-di-tert-butyldiazadiene, on the other hand, a 1/1 complex **4** with dimethyl acetylene dicarboxylate was isolated.

The complexes **2–4** can be readily characterized by their NMR spectra. The substituents on the dad are helpful in determining the total symmetry. The ^{1}H chemical shifts of the alkyl group of the ester substituents in **2** are separated by 0.6 to 0.9 ppm in the case of o-substituted N-aryl group. This is due to the anisotropic ring current of the tilted aryl group, the high field signal coming from the ester substituent in α-position to the metal. For **2d** and **2e** this chemical shift difference is much smaller. In complex **3** the ester CH_2 signal has the same chemical shift as the β-CH_2 signal in the complexes **2b** or **2f**. The isopropyl ester complex **2g** exhibits the largest $\Delta\delta$-value (1.17 ppm) for the CH signals in α- and β-position, respectively, which further supports the α/β-assignments.

In the case of complex **4** there is, of course, only one ^{1}H signal for the ester methyl groups. The composition of this complex is clear not only from the integrated NMR spectrum but also from the IR spectrum. The coordinated triple bond gives rise to an IR-active vibration at 1795 cm^{-1}, whereas no such band appears for any of the alkyne-derived complexes **2, 3**, in which the coupling to the butadienediyl moiety has occurred. Their quaternary C atoms show ^{13}C-resonances at ca 146 and 145 ppm. One complex of type **2** was prepared previously by Ito et al., but not fully characterized [12].

Synthesis of platinacyclopentadienes

Although it was expected that platinum complexes would be less reactive in catalysis than their palladium analogues (see below), we also tried to synthesize platinacyclopentadienes. Since the reduction of (dad)$PdCl_2$ in the presence of alkynes gave no isolable products of type **2**, we did not repeat the experiment with (dad)$PtCl_2$, but started off immediately with bis(dibenzylideneacetone)platinum. In dichloromethane in the presence of the acetylenic ester and the dad, the colour of Pt(dba)$_2$ changed from violet to a dark red. The stable (dad)platinacyclopentadienes

5 were isolated in reasonable yield.

(1) (5)
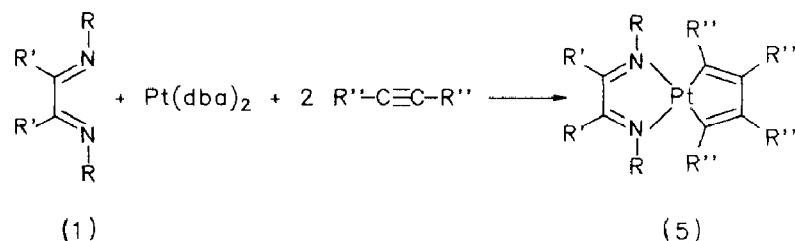
	R	R′	R″
5a	$2,6\text{-}Me_2C_6H_3$	H	$COOCH_3$
b	$2,6\text{-}Me_2C_6H_3$	CH_3	$COOCH_3$
c	$2,6\text{-}Me_2C_6H_3$	H	$COOCH_2CH_3$
d	$2,6\text{-}(^ipr)_2C_6H_3$	H	$COOCH_3$

The complexes **5** are quite stable toward oxygen, even in solution. They are red in comparison to the orange Pd complexes, but otherwise fully analogous to the latter. Their ^{1}H and ^{13}C NMR spectra underline this similarity. Although **5** are unreactive in catalytic experiments with alkynes (see below) they are excellent precursors for the synthesis of new platinacycles from various C=C double bond systems [13].

Catalytic reactions with palladacyclopentadienes

A thermal reaction of **2** with one equivalent of acetylenedicarboxylic acid esters in toluene at 80°C gave the hexaesters of mellitic acid **6** (benzene hexacarboxylic acid). Free dad and metallic palladium were further products. This stoichiometric reaction also occurred with propiolic ester (**7**) and with phenylacetylene (**8**).

(6) (7) (8)
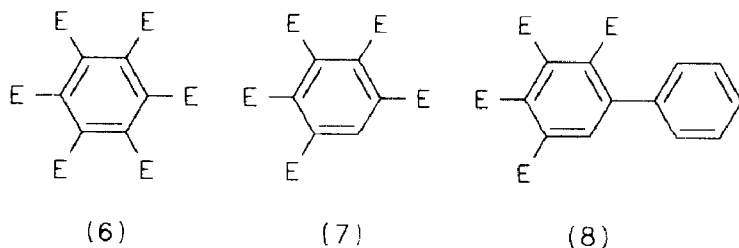
E = COOR″

The first catalytic studies showed that acetylenedicarboxylic acid esters and propiolic acid esters could be cyclotrimerized with **2** as a catalyst in high yield, whereas phenylacetylene alone did not react, although the formation of product **8** showed that there is an interaction between **2** and this alkyne. No oligomers were formed from propargylic alcohols and ethers alone. As expected, a mixture of EC≡CE, C_6H_5C≡CH and **2** (100/100/1) gave the cooligomer **8** in a catalytic reaction. From the reaction mixture, after 25 cycles, **2** was recovered. Obviously **2** is reformed quickly after the reductive elimination of the aromatic product. It seemed promising to investigate the possibility of a preferential reaction of a second alkyne with the always quickly reformed complex **2**.

A number of alkynes were treated with dimethylacetylene dicarboxylate (dmad) (1/2) in the presence of **2c** (0.04 equiv.) in toluene at 80°C. The table shows that

Table 1

Yields of 1:2-cyclotrimers of alkynes RC≡CR' with dmad relative to those of the dmad-cyclotrimer **6**

Alkyne		No	(%)	6
R	R'			(%)
Et	Et	**10**	16	84
H	Bu	**11**	9	91
SiMe$_3$	SiMe$_3$	**12**	10	90
Ph	Ph	**13**	15	85
MeOCH$_2$	MeOCH$_2$	**14**	40	60
H	MeOCH$_2$	**15**	10	90
H	COOEt	**7b**	35	65
H	COO^{i}Pr	**7c**	28	72
H	COO^{t}Bu	**7d**	10	90
C$_6$H$_5$	SiMe$_3$	**16**	52	48
H	C$_6$H$_5$	**8**	45 [a]	–
H	CMe$_2$OC	**17**	100	–
SiMe$_3$	CH$_2$OH	**18**	100 [b]	–
H	CH(Ph)OC	**19**	100	–
COOCH$_3$	CO$_2$CH$_2$C≡CH	**20**	100	–
COOCH$_3$	CO$_2$CH$_2$C≡CH	**21**	100	– [c]

[a] The linear products **9a** and **9b** were formed in 46% yield. [b] 3:1 cyclo-cotetramer 35% [14]. [c] Without addition of dmad.

cyclo-cotrimerization occurs to a varying extent. Since these were only screening experiments, giving the final product ratios after a time of approximately 12 h, the factors favouring cooligomerization are not yet well understood. Steric influences can be seen in the case of the three propiolic esters. On the other hand very bulky acetylenes such as bis(trimethylsilyl)acetylene are incorporated. Very efficient cooligomerization occurs with 2-butyne-1,4-diol, and even more so with 1-phenyl-2-trimethylsilylacetylene. With propargylic alcohols and EC≡CE there is a trans-esterification during the reaction [14]. The same type of reaction occurs with 1-phenyl-2-propyn-1-ol. The preformed ester of acetylenedicarboxylic acid with propargylic alcohol reacts even faster to give the "mixed" aromatic compound.

No mellitic acid ester was formed in the co-reaction of phenylacetylene and dmad. But along with the aromatic 1,2-product **8**, mentioned earlier, two other products of the same molecular mass were separated by column chromatography (**9a**, **9b**). By NMR spectroscopy they were identified as the two linear 1/2-products with (E)- and (Z)-configuration. This is of relevance for the mechanism of the cyclo-(co)trimerization.

The C≡C triple bound can insert into a Pd–C bond to form a palladacycloheptatriene intermediate **A**, from which **8** is reductively eliminated. Alternatively, the C–H bond of the acetylene can add to a Pd–C bond to give the vinyl-hydrido intermediate **B**. Reductive elimination affords the dienynes **9** (Scheme 1). The allenyl-carbene-type mesomeric structure **B'** could account for the fact that the (E)-isomer **9b** is also found. From intermediate **B** formation only of the (Z)-isomer **9a** is conceivable. The palladacycloheptatriene intermediate **A** cannot lead to the acyclic products **9** because the hydrogen atom in a β-position of this nonplanar heterocycle is trans to the Pd atom and also far away from the α'-position, too. It
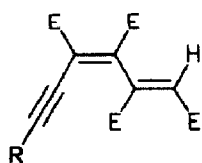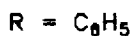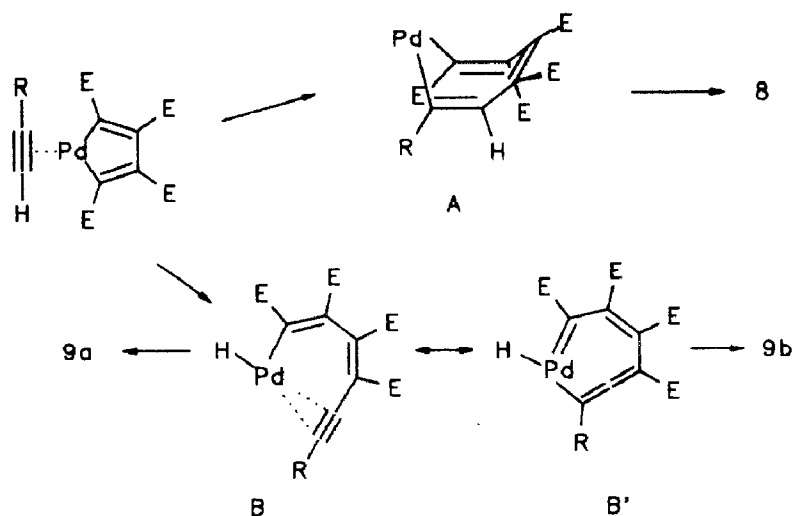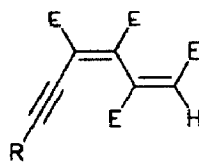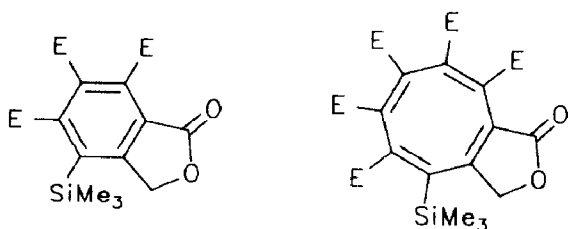
Scheme 1.

should finally be noted that acyclic products of cooligomerization reactions with a terminal alkyne may have been overlooked in earlier experiments.

Conclusions

The palladacyclopentadienes **2** are very stable complexes. Therefore, a catalytic reaction is improbable unless there is an activation step. This activation energy could be provided by the energy connected with the formation of an aromatic compound, but this would be an extreme case. In the formation of the acyclic products **9** from **2** and an alkyne there is no net change in the number of double and triple bonds. Another interesting example is the formation of a cyclooctatetraene [14] in the reaction of a propargylic alcohol and dmad, parallel to the formation of the benzolactone (Table 1). Both atypical reactions would, of course, be impos-

2   4
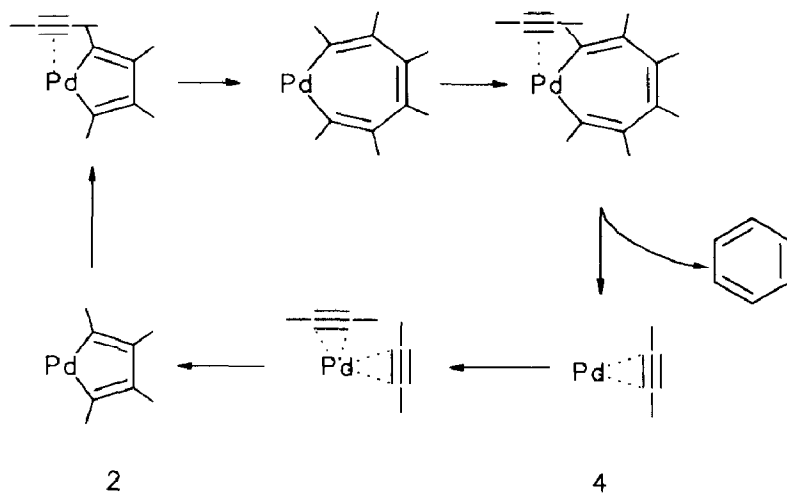
Scheme 2.

sible if a Diels–Alder-type intermediate were involved [4,15]. But all the products and by-products are compatible with an addition of or to a Pd–C bond. Prior to the reductive elimination of any moiety with two σ-bonds to Pd, another alkyne molecule is probably coordinated. Such an intermediate would be structurally very similar to the early phase of the transformation (Pd-cyclopentadiene → Pd-cycloheptadiene) on the one hand, and since the barrier to reductive elimination is obviously not too high, the intermediate is energetically not too far from the η^2-alkyne complex of type **4**. The relative stability of the Pd-cyclopentadiene **2** therefore stems from the fact that no simple elimination is possible (Scheme 2).

An important point in this discussion should be underlined, namely that complexes **2** are clearly Pd^{II} compounds. Both **2, 3** and **4** are only accessible in the case of very electron-deficient alkynes. Thus **4** can also be called a palladacyclopropene. Intermediate addition of electron-deficient alkynes to the three $Pd(\sigma\text{-}C)_2$ complexes in the scheme could, in valence bond terms, be described as oxidative addition to give Pd^{IV}. Thus there is no way of distinguishing throughout the whole catalytic cycle between a $Pd^{IV}\text{-}Pd^{II}$ process and a $Pd^{II}\text{-}Pd^0$ process. The assumption that at some stage a complex of type **4** must be an intermediate suggested the possibility of intercepting this complex with other competitive multiple bond systems. Subsequent papers will deal with reactions of allylic alcohols, allenes, vinyl ethers, and strained or normal alkenes [13].

Experimental

All manipulations were carried out under nitrogen, although the new compounds turned out to be rather stable towards air or moisture. IR spectra: Perkin Elmer spectrograph 325 or 577 or Pye Unicam SP 1100; NMR spectra: Bruker WP 80 SYFT and AM 360; mass spectra: Varian CH 7. Microanalyses were performed in the Analytical Service of our departement of Applied and Analytical Chemistry on a Carlo Erba machine.

The syntheses of dad have been described earlier [16]. Acetylenedicarboxylic acid dimethyl and diethyl ester, phenylacetylene, 1-hexyne, 3-hexyne and bis(trimethyl-silyl)acetylene were purchased. Other alkynes were prepared by published procedures [17]. Bis(dibenzylidene acetone)palladium was prepared as previously described [18].

2-Butynedioic acid di-2-propynylester was prepared by a modified synthesis described in a patent by L.A. Miller [19]. A mixture of 10.3 g (90 mmol) acetylenedicarboxylic acid, 10.4 g (180 mmol) of propargylic alcohol and 1 g p-toluene sulfonic acid in 100 ml of benzene was stirred under reflux under a Dean-Stark trap for 14 h. After the separation of 3.2 ml of water the mixture was cooled and 100 ml of diethyl ether were added. The solution was washed with aqueous $NaHCO_3$ (10%) and then with water until neutral. After drying of the solution over $MgSO_4$ and filtration, all solvents and low boiling materials were removed. Distillation of the crude oil in vacuo (10^{-3} mbar) gave 8.6 g (52%) of the product. IR (Nujol): ν 2100 (w, C≡C) cm^{-1}. ^{1}H NMR ($CDCl_3$): 4.83 (d, CH_2, 4H); 2.63 (t, CH, 2H).

The methyl-2-propynylester was prepared accordingly.

Synthesis of palladacyclopentadienes (2). About 1.03 g (1.8 mmol) of $Pd(dba)_2$ and 2 mmoles of the corresponding dad were dissolved in 150 ml of acetone, and 500 mg (3.6 mmol) of acetylenedicarbonic acid dimethylester (dmad) added dropwise. The colour changed from dark violet to brown or orange. After 3 h stirring at room temperature the solution was concentrated to about 30 ml, then kept at $-20\,°C$, at which most of the complex **2** crystallized out. Further, less pure crops were isolated from the mother liquid. The fine red crystals were collected, washed with diethyl ether, and dried in vacuo. Recrystallization was from CH_2Cl_2/Et_2O.

2,3,4,5-Tetrakis(carbomethoxy)-spiro-glyoxalbis(2,6-dimethylphenylimine)pallada-cyclopenta-2,4-diene (2a). Yield 1.02 g (88%). ^{1}H NMR ($CDCl_3$): δ 8.10 (s, N=CH, 1H); 7.12 (s, H(Ph), 3H); 3.48 (s, OCH_3, 3H); 2.85 (s, OCH_3, 3H); 2.29 (s, CH_3(Ph), 6 H). ^{13}C NMR ($CDCl_3$): δ 170 (C=N); 165.8, 163.6, 161.7 (2 C=O, 2 NC_{Ph}); 146.5, 145.4 (2 $C\ CO_2$); 129.5, 128.4, 127.3 (C(Ph)); 51.1, 50.9 (2 CO_2CH_3); 18.5 (CH_3(Ph)). IR (KBr): ν 1700 (C=O); 1215 (C–O) cm^{-1}. Analysis. Found C 55.15; H 5.18; N 4.17. $C_{30}H_{32}N_2O_8Pd$ (654.95) calcd.: C 55.01, H 4.89; N 4.28%.

2,3,4,5-Tetrakis(carboethoxy) analogue (2b). Yield 1.02 (79%). IR (KBr): ν 1693 (C=O); 1215 (C–O) cm^{-1}. ^{1}H NMR (acetone-d$_6$): δ 8.42 (s, N=CH, 1H); 7.13 (s, H_{Ph}, 3H); 3.92 (q, OCH_2, 2H); 3.06 (q, OCH_2, 2H); 2.30 (s, CH_3(Ph), 6H); 1.10 (t, CH_3, 3H); 0.95 (t, CH_3, 3H). Analysis. Found C 58.75; H 5.96; N 3.87. $C_{34}H_{40}N_2O_8Pd$ (711.11) calcd.: C 57.43, H 5.63, N 3.94%.

Tetrakis(carbomethoxy) derivative with glyoxalbis(2,6-diisopropylphenylimine) (2c). Yield 789 mg (74%). ^{1}H NMR ($CDCl_3$): δ 8.11 (s, N=CH, 1H); 7.25 (s, H(Ph), 3H); 3.46 (s, OCH_3, 3H); 3.21 (sept, CH_{iso}, 2H); 2.74 (s, OCH_3, 3H); 1.06, 1.42 (2 d, $CH_{3(iso)}$, 12H). ^{13}C NMR ($CDCl_3$): δ 170.5, 164.2, 163.5, 161.8 (2 C=O, 2 NC(Ph), 2 N=CH); 145.4, 144.7 (2 $C\ CO_2$); 140.1, 128.0, 123.6 (C(Ph)); 51.0, 50.7 (2 CO_2CH_3); 28.7 (CH_{iso}); 25.2, 21.9 (2 CH_3). IR(KBr): ν 1700 (C=O); 1220 (C–O) cm^{-1}.

Glyoxalbis(p-tolylimine) derivative (2d). After 30 min of stirring a yellow precipitate is formed. Concentration to 15 ml gives **2d** as a yellow powder in 94% yield. ^{1}H NMR ($CDCl_3$): δ 8.35 (s, N=CH, 1H); 7.10 (s, H(Ph), 3H); 3.70 (s, OCH_3, 3H); 3.33 (s, OCH_3, 3H) 2.25 (s, CH_3, 3H). IR (KBr): ν 1700 (C=O); 1210 (C–O) cm^{-1}.

Glyoxalbis(p-anisylimine) derivative (2e). The product from the diethyl ester

(dead) was obtained as a yellow powder in 64% yield. ^{1}H NMR (acetone-d$_6$): δ 8.35 (s, N=CH, 1H); 7.3 (s, H(Ph), 3H); 4.17 (q, OCH$_2$, 2H); 3.80 (q, partly hidden underneath OCH$_3$); 3.71 (s, OCH$_3$, 3H); 1.26 (t, CH$_3$, 3H); 1.01 (t, CH$_3$, 3H). IR (KBr): ν 1708 (C=O); 1254, 1208, 1167 (C–O) cm^{-1}.

Biacetylbis(2,6-dimethylphenylimine) derivative (2f). The product from dead was obtained as orange-red crystals in 76% yield after recrystallization. ^{1}H NMR (acetone-d$_6$): δ 7.11 (s, H(Ph), 3H); 3.89 (q, OCH$_2$, 2H); 3.15 (q, OCH$_2$, 2H); 3.15 (q, OCH$_2$, 2H); 2.24 (s, CH$_3$(Ph), Ph); 2.13 (s, CH$_3$C=N, 3H) 1.09 (t, CH$_3$, 3H); 0.92 (t, CH$_3$, 3H). ^{13}C NMR (CDCl$_3$): δ 175.1 (C=N); 170.6, 163.6, 161.0 (2 C=O, 2 NC(Ph)); 145.8, 144.2 (2 CCO$_2$); 128.8, 128.4, 126.6 (C(Ph));59.7, 59.6 (2 CH$_2$); 19.4 (CH$_3$C=N); 18.3 (CH$_3$(Ph)); 14.0, 13.5 (2 CH$_3$CH$_2$). IR (KBr): ν 1690 (C=O); 1220 (C–O) cm^{-1}.

Tetrakis(carboisopropoxy) analogue (2g). The yellow isopropoxy derivative was obtained in 69% yield. ^{1}H NMR (acetone-d$_6$): δ 7.13 (s, H(Ph), 3H); 4.73 (sept, CH$_{iso}$, 1H); 3.56 (sept, CH$_{iso}$, 1H); 2.27 (s, CH$_3$(Ph), 6H); 2.11 (s, CH$_3$C=N, 3H) 1.13 (d, CH$_{3(iso)}$, 6H); 0.93 (d, CH$_{3(iso)}$, 6H). ^{13}C NMR (CDCl$_3$): δ 174.6 (C=N); 169.6, 163.5, 160.1 (2 C=O, 2 NC(Ph)); 146.6, 144.7 (2 CCO$_2$); 128.8, 128.5, 126.5 (C(Ph)); 67.4, 67.1 (2 CH$_{iso}$); 21.9, 21.4 (2 CH$_{3(iso)}$); 19.4 (CH$_3$C=N); 18.5 (CH$_3$(Ph)). IR (KBr): ν 1692 (C=O); 1220 (C–O) cm^{-1}.

Biacetylbis(2,6-diisopropylphenylimine) derivative (2h). The orange-red product from dmad was obtained, after recrystallization from CH$_2$Cl$_2$/Et$_2$O, in 68% yield. ^{1}H NMR (CDCl$_3$): δ 7.27 (s, H$_{Ph}$, 3H); 3.50 (s, OCH$_3$, 3H); 3.16 (sept, CH$_{iso}$, 2H); 2.84 (s, OCH$_3$, 3H); 1.99 (s, CH$_3$C=N, 3H), 1.45, 1.08 (2 d, CH$_{3(iso)}$, 12H). ^{13}C NMR (CDCl$_3$): δ 175.5 (C=N), 170.6, 164.2, 161.5 (2 C=O, 2N C(Ph)); 145.5, 142.6 (2 CCO$_2$); 138.9, 127.5, 124.2 (C(Ph)); 51.1 (2 CO$_2$CH$_3$); 29.3 (CH$_{iso}$); 24.1, 22.9 (2 CH$_{3(iso)}$); 22.1 (CH$_3$C=N). IR (KBr): ν 1700 (C=O); 1215 (C–O) cm^{-1}.

3,4-Dicarboethoxy-spiro-biacetylbis(2,6-diisopropylphenylimine)palladacyclopenta-diene (3). By analogy to the preparation of **2**, Pd(dba)$_2$ (1.2 g, 2.1 mmole), the dad (1.06 g, 2.6 mmole) and propiolic acid ethyl ester (0.5 ml, 4.5 mmole) were brought into reaction in 150 ml of acetone. After 24 h stirring the very dark solution was evaporated to dryness and the residue was dissolved in CH$_2$Cl$_2$ (10 ml). Diethyl ether was added and the mixture cooled overnight. A dark precipitate formed was separated and recrystallized (CH$_2$Cl$_2$/Et$_2$O). Yield 125 mg (8.5%). ^{1}H NMR (CDCl$_3$): δ 7.30 (s, H(Ph), 3H); 6.87 (s, Pd CH, 1H); 3.96 (q, COCH$_2$, 2H); 2.97 (sept, CH$_{iso}$, 2H); 2.13 (s, CH$_3$C=N, 3H); 1.30, 1.17 (2 d, CH$_3$, 12H); 1.10 (t, CH$_3$, 3H). IR (KBr): ν 1695 (C=O); 1215 (C–O) cm^{-1}.

(η^2-Acetylenedicarboxylic acid dimethyl ester)glyoxalbis(tert-butylimine)palladium (4). The components Pd(dba)$_2$ (1.06 g, 1.85 mmole), dad (0.32 g, 1.90 mmole), dmad (0.27 g, 1.90 mmole) were allowed to react in 150 ml of acetone. After 24 h stirring at room temperature the solution was evaporated and 15 ml of CH$_2$Cl$_2$ and 80 ml of Et$_2$O were added. Orange, bar-shaped crystals separated when the solution was kept overnight at $-20\,^\circ$C. They were collected, washed with Et$_2$O, and dried in vacuo. Yield 390 mg (51%). ^{1}H NMR (CDCl$_3$): δ 8.20 (s, N=CH, 1H); 3.82 (s, OCH$_3$, 3H); 1.50 (s, CH$_3$, 9H). IR (KBr): ν 1795 (C≡C); 1675 (C=O); 1200 (C–O) cm^{-1}.

2,3,4,5-Tetrakis(carbomethoxy)-spiro-glyoxalbis(2,6-dimethylphenylimine)platina-cyclopenta-2,4-diene (5a). A mixture of 760 mg (1.14 mmole) of Pt(dba)$_2$, 317 mg (1.20 mmole) of the dad, of 345 mg (2.4 mmole) of dmad (added dropwise) in 60 ml

of dichloromethane was stirred for 16 h at room temperature during which the colour changed from dark violet to dark red. The volume was reduced to 5 ml and 20 ml of diethyl ether were added. The solution was kept at $-22\,^{\circ}$C to give 420 mg (48%) of red crystals. ^{1}H NMR (CDCl$_3$): δ 8.72 (s, N=CH, 1H); 7.17 (s, H(Ph), 3H); 3.53 (s, OCH$_3$, 3H); 2.94 (s, OCH$_3$, 3H); 2.32 (s, CH$_3$(Ph), 6H). ^{13}C NMR (CDCl$_3$): δ 171.3, 164.6 (2 C=O);166.9 (HC=N); 147.1, 146.6, 145.1 (2 NC(Ph), 2 CCO$_2$); 130.3, 128.4, 127.8 (C(Ph)); 51.2 (2 CO$_2$CH$_3$); 18.4 (CH$_3$(Ph)). IR (KBr): ν 1720, 1714, 1700 (C=O); 1220 (C–O) cm^{-1}.

Biacetylbis(2,6-dimethylphenylimine) derivative (5b). The preparation was similar to that of **5a**. After the concentration of the solution the product was precipitated with diethyl ether. The supernatant liquid was decanted and the residue washed with Et$_2$O, and dried in vacuo. Yield of crude product 73%. ^{1}H NMR (CDCl$_3$): δ 7.15 (s, H(Ph), 3H); 3.49 (s, OCH$_3$, 3H); 2.97 (s, OCH$_3$, 3H); 2.23 (s, CH$_3$(Ph), 6H); 1.73 (s, CH$_3$ C=N; 3H). IR (KBr): ν 1721 (C=O); 1227 (C–O) cm^{-1}.

Tetrakis(carboethoxy) derivative (5c). The preparation was analogous to that of **5a** and the red powder was obtained in 51% yield. ^{1}H NMR (acetone-d$_6$): δ 8.72 (s, N=CH, 1H); 7.13 (s, H(Ph), 3H); 3.93 (q, OCH$_2$, 2H); 3.14 (q, OCH$_2$, 2H); 2.29 (s, CH$_3$(Ph), 6H); 1.09 (t, CH$_3$, 3H); 1.00 (t, CH$_3$, 3H). ^{13}C NMR (CDCl$_3$): δ 171.0, 164.3 (2 C=O); 167.2 (HC=N); 147.3, 144.7, 143.2 (2 NC(Ph), 2 CCO$_2$); 130.3, 128.4, 127.6 (C(Ph)); 59.8 (2 CO$_2$CH$_2$); 18.4 (CH$_3$(Ph)); 14.0, 13.6 (CH$_2$CH$_3$). IR (KBr): ν = 1715, 1695 (C=O); 1228 (C–O) cm^{-1}.

Glyoxalbis(2,6-diisopropylphenylimine) analogue (5d). The synthesis was similar to that of **5a**; the orange-red powder was obtained in 45% yield. ^{1}H NMR (CDCl$_3$): δ 8.70 (s, N=CH, 2H); 7.25, 7.20 (2 s, H(Ph), 6H); 3.50 (s, OCH$_3$, 6H); 3.25 (sept, CH$_{iso}$, 4H); 2.85 (s, OCH$_3$, 6H); 1.45, 1.05 (2 d, CH$_{3(iso)}$, 24H).

Catalytic co-cyclization of alkynes with dialkyl acetylenedicarboxylates

The catalyst (**2**) and a 10 to 100-fold excess of an alkyne RC≡CR′ were dissolved in 100 ml of toluene and two molar equivalents of the acetylenic ester were added when the mixture had been warmed to the reaction temperature (50–80 $^{\circ}$C). The progress of this reaction was monitored by TLC. After 3–24 h the more volatile material was evaporated off and the residue separated by column chromatography (aluminium oxide activity II or silicagel).

Mellitic acid hexamethyl ester (6a). The iso-cyclotrimerization (catalyst **2c**) of acetylenedicarboxylic acid dimethyl ester (dmad) gave a 98% yield, after 3 h at 60 $^{\circ}$C. Separation from catalyst residues by chromatography on Al$_2$O$_3$, with hexane/ethylacetate 5/4 as eluent followed by recrystallization from methanol gave colourless crystals of **6a**. ^{1}H NMR (CDCl$_3$): δ 3.88 (s, OCH$_3$). ^{13}C NMR (CD$_3$OD): δ 166.5 (C=O); 135.4 (C(Ph)); 54.2 (OCH$_3$). IR (KBr): ν 1745 (C=O); 1270–1220 (C–O) cm^{-1}.

Mellitic acid hexaethyl ester (6b). Use of catalyst **2c** and a 100-fold excess of the acetylenic diethyl ester gave a 95% yield of **6b**. ^{1}H NMR (CDCl$_3$): δ 4.40 (q, CH$_2$); 1.45 (t, CH$_3$).

Pentakis(carbomethoxy)benzene (7a). A stoichiometric reaction of **2c** with propiolic acid methyl ester for 4 h gave **7** which was chromatographed with hexane/ethylacetate 8/2 as eluent. White crystals were obtained from MeOH in 25% yield. The mass spectrum (70 eV) showed the M^+ peak (368). ^{1}H NMR (CDCl$_3$): δ 8.65 (s, CH, 1H); 3.95 (s, 4 OCH$_3$, 12H); 3.88 (s, OCH$_3$, 3H). IR

(KBr): ν 1760, 1752, 1730 (C=O); 1258 (C–O) cm^{-1}. The catalytic reactions of **2c** with dmad and various propiolic acid alkyl esters were carried out with a 25-fold excess of the alkynes. The reaction temperatures ranged from 50 to 80 °C. After 1 d the mixture were separated by column chromatography with ether/hexane 4/1 as eluent.

1-Carboethoxy-2,3,4,5-tetrakis(carbomethoxy)benzene (7b). ^{1}H NMR (CDCl$_3$): δ 8.60 (s, CH(Ph), 1H); 4.40 (q, CH$_2$, 2H); 3.97, 3.89 (2 s, 4 OCH$_3$, 12H); 1.40 (t, CH$_2$CH$_3$, 3H).

1-Carboisopropoxy-2,3,4,5-tetrakis(carbomethoxy)benzene (7c). ^{1}H NMR (CDCl$_3$): δ = 8.60 (s, CH(Ph), 1H); 5.30 (sept, CH$_{iso}$, 1H); 4.0, 3.96 (2 s, 4 OCH$_3$, 12H); 1.35 (d, CH$_{3(iso)}$, 6H).

1-Carbo(tert-butoxy)-2,3,4,5-tetrakis(carbomethoxy)benzene (7d). ^{1}H NMR (CDCl$_3$): δ 8.60 (s, CH(Ph), 1H); 4.0, 3.97, 3.94, 3.91 (4 s, 4 OCH$_3$, 12H); 1.60 (s, CH$_3$, 9H).

2,3,4,5-Tetrakis(carbomethoxy)biphenyl (8). A stoichiometric reaction between (**2c**) and phenylacetylene gave **8** in 76% yield. From a catalytic reaction the isolated yield was 40%; an *E/Z*-mixture of **9a/b** was obtained in 46% yield. Separation was by column chromatography. **8**: ^{1}H NMR (CDCl$_3$): δ 8.07 (s, CH(Ph), 1H); 7.47 (s, CH(Ph), 5H); 3.92, 3.88, 3.86, 3.63 (4 s, 4 OCH$_3$, 12H). ^{13}C NMR (CDCl$_3$): δ 167.4 (2 C=O); 165.7, 164.9 (2 C=O); 142.2, 138.0, 136.7, 134.0, 130.2, 130.1 (C$_{ipso}$); 134.0, 128.5, 128.2 (CH); 53.2, 53.0, 52.9, 52.5 (OCH$_3$). IR (KBr): ν 1745–1729 (C=O); 1309, 1280, 1254, 1235, 1205, 1168 (C–O) cm^{-1}. MS (70 eV): m/z (%) = 386 (*M*$^+$; 20); 355 (M$^+$ – OCH$_3$; 100); 328 (8); 180 (6); 119 (12). *1,2,3,4-Tetracarbomethoxy-6-phenyl-hexa-1,3-dien-5-yne (9a/9b):* The yield from the reaction described above was 450 mg (46%). (*Z*)-isomer **9a**: ^{1}H NMR (CDCl$_3$): δ 7.48, 7.44 (2 s, CH(Ph), 5); 6.59 (s, CH$_{olef(z)}$, 1); 3.86, 3.79, 3.74 (3 s, 4 OCH$_3$, 12). (*E*)-isomer **9b**: ^{1}H NMR (CDCl$_3$); δ 7.48, 7.44 (2 s, CH(Ph), 5); 7.09 (s, CH$_{olef(E)}$, 1); 3.86, 3.79, 3.74 (3 s, 4 OCH$_3$, 12). IR (KBr): ν 2980 (C H); 2170 (C≡C); 1720 (C=O); 1225 (C–O) cm^{-1}. MS (70 eV): m/z (%) = 386 (*M*$^+$; 20); 355 (*M*$^+$ – OCH$_3$; 13); 327 (*M*$^+$ – COOCH$_3$; 99); 297 (19); 205 (17); 105 (61); 57 (100); 43 (55).

1,2,3,4-Tetrakis(carbomethoxy)-5,6-diethylbenzene (10). The catalytic cooligomerization was carried out at 80 °C with **2c** as catalyst with a 25-fold excess of 3-hexyne and dmad in 70 ml of toluene. After 22 h the product mixture was separated by column chromatography with ether/hexane 4/1 as eluent. ^{1}H NMR (CDCl$_3$): δ 3.95, 3.87 (2 s, OCH$_3$, 12H); 2.70 (q, CH$_2$, 2H); 1.25 (t, CH$_3$, 6H). IR (KBr): ν 1755-1725 (C=O); 1270-1205 (C–O) cm^{-1}.

1,2,3,4-Tetrakis(carbomethoxy)-n-butylbenzene (11). The reaction conditions were analogous to those used for **10**. ^{1}H NMR (CDCl$_3$): δ = 7.95 (s, CH$_{Ph}$, 1H); 3.96, 3.94, 3.89, 3.87 (4 s, 4 OCH$_3$, 12H); 2.70 (q, CH$_2$, 2H); 1.4 (m$_{br}$, 2 CH$_2$, CH$_3$, 7H). IR (KBr): v = 1740 (C=O); 1270 (C-O) cm^{-1}.

1,2,3,4-Tetrakis(carbomethoxy)-5,6-bis(trimethylsilyl)benzene (12). The catalysis was performed as described above. ^{1}H NMR (CDCl$_3$): δ 3.87, 3.84 (2 s, 4 OCH$_3$, 12H); 0.4 (s, 2 SiCH$_3$, 18H).

3,4,5,6-Tetrakis(carbomethoxy)-o-terphenyl (13). The product was obtained from tolane (diphenylacetylene) and dmad in 56% yield. ^{1}H NMR (CDCl$_3$): δ 7.15 (m, br, CH(Ph), 10H); 3.90 (s, 2 OCH$_3$, 6H); 3.50 (s, 2 OCH$_3$, 6H). IR (KBr): ν = 1740 (C=O); 1255, 1215 (C–O) cm^{-1}.

1,2,3,4-Tetrakis(carbomethoxy)-5,6-bis(methoxymethyl)benzene (14). The proce-

dure was analogous to that used for **10**, except that for the separation of **6a** and **14** hexane/ether 1/10 was used as eluent. ^{1}H NMR (CDCl$_3$): δ 4.50 (s, CH$_2$, 4H); 3.90 (s, 2 OCH$_3$, 6H); 3.80, 3.77 (2 s, 2 OCH$_3$, 12H); 3.15 (s, CH$_2$OCH$_3$, 6H). IR (KBr): ν 1745 (C=O); 1250 (C–O) cm^{-1}.

1,2,3,4-Tetrakis(carbomethoxy)-5-methylmethoxybenzene (15). The catalyst to alkyne ratio was the same as for **10**. Heating to 50°C was continued for 24 h; for separation of the products **6a** and **15** hexane/ether 1/7 was used as eluent. ^{1}H NMR (CDCl$_3$): δ 8.20 (s, CH(Ph), 1H); 4.60 (s, CH$_2$, 4H) 3.94, 3.90, 3.89, 3.87 (4 s, 4 OCH$_3$, 12H); 3.38 (s, CH$_2$OCH$_3$, 3H). IR (KBr): ν 1740 (C=O); 1255 (C–O) cm^{-1}.

2-Trimethylsilyl-3,4,5,6-tetrakis(carbomethoxy)biphenyl (16). By use of catalyst (**2c**), a 12.5-fold excess of the phenyltrimethylsilylacetylene and the double molar quantity of dmad, the cotrimer **16** is obtained in the usual way. ^{1}H NMR (CDCl$_3$): δ 7.40 (m, CH(Ph), 5H); 3.92, 3.90 (2 s, 3 OCH$_3$, 9H); 3.50 (s, OCH$_3$, 3H); –0.15 (s, Si(CH$_3$), 9H). IR (KBr): ν 1770–1730 (C=O); 1260 (Si–C); 1230–1215 (C–O) cm^{-1}.

3,3-Dimethyl-5,6,7-tris(carbomethoxy)-2(3H)benzofuranon (17). Reaction of 25-fold excess of 3-methyl-1-butyne-3-ol and the two molar proportion of dmad was carried out with **2c** as catalyst. The sole catalytic product **17** was separated by column chromatography with ether/hexane 4/1 as eluent. ^{1}H NMR (CDCl$_3$): δ 7.92 (s, CH(Ph), 1H); 4.05, 3.97, 3.92 (3 s, 3 OCH$_3$, 9H); 1.75 (s, 2 CH$_3$, 6H). IR (KBr): ν 1775 (C=O$_{lac}$); 1740 (C=O); 1255 (C–O) cm^{-1}.

4-Trimethylsilyl-5,6,7-tris(carbomethoxy)-2(3H)benzofuranon (18). The preparation was as described earlier [14]. ^{1}H NMR (CDCl$_3$): δ 7.92 (s, CH(Ph), 1H); 4.05, 3.97, 3.95 (3 s, 3 OCH$_3$, 9H); 1.75 (s, C CH$_3$, 9H). IR (KBr): ν 1778–1725 (C=O) cm^{-1}.

3-Phenyl-5,6,7-tris(carbomethoxy)-2(3H)benzofuranon (19). The catalyst to alkyne ratio was 1/12.5/25. The product **19** was obtained in 42% yield. ^{1}H NMR (CDCl$_3$): δ 7.80 (d, CH(Ph), 1H; ^4J(H(Ph)H(lac)) = 0.8 Hz); 7.42 (m, CH(Ph), 5H); 6.42 (D, CH(lac), 1H; ^4J(H(lac)H(Ph)) = 0.7 Hz); 4.03, 3.92, 3.89 (3 s, 3 OCH$_3$, 9H). IR(KBr): ν 1780 (C=O$_{lac}$); 1750, 1730 (C=O$_{ester}$); 1270, 1250, 1205 (C–O) cm^{-1}.

5,6,7-Tris(carbomethoxy)-2(3H)benzofuranon (20). ^{1}H NMR (CDCl$_3$): δ 8.04 (s, CH(Ph), 1H); 5.35 (s, CH$_2$(lac), 2H); 3.96, 3.83 (2 s, 3 OCH$_3$, 9H). IR (KBr): ν 1780 (C=O$_{lac}$); 1720 (C=O); 1290–1225 (C–O) cm^{-1}.

6(5),7-Bis(carbomethoxy)-5(6)-(carbo-2-propynoxy)-2(3H)benzofuranon (21). By use of a 10-fold excess of the propargylic ester, the codimer **20** was obtained in 50% yield after 3 d at room temperature. ^{1}H NMR (CDCl$_3$): δ 8.00 (s, br, CH(Ph), 1H); 5.35 (s, br, CH(lac), 2H); 4.90 (d, CH$_2$(propyn), 2H); 3.97, 3.89 (2 s, 2 OCH$_3$, 6H); 2.54 (t, CH$_{propyn}$, 1H). IR (KBr): ν 1770 (C=O$_{lac}$); 1725 (C=O$_{ester}$); 1280, 1255, 1210 (C–O) cm^{-1}. MS (70 eV): m/z (%) 332 (M^+; 12); 277 (M^+ – HCCH$_2$O; 100%); 205 (10); 160 (6); 149 (8); 71 (14); 57 (20); 43 (8).

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