Novel Three-Component Coupling Using Aluminum Tris(2,6-diphenylphenoxide) (ATPH): The Same Synthetic Strategy Leads to *trans*- and *cis*-Jasmonates

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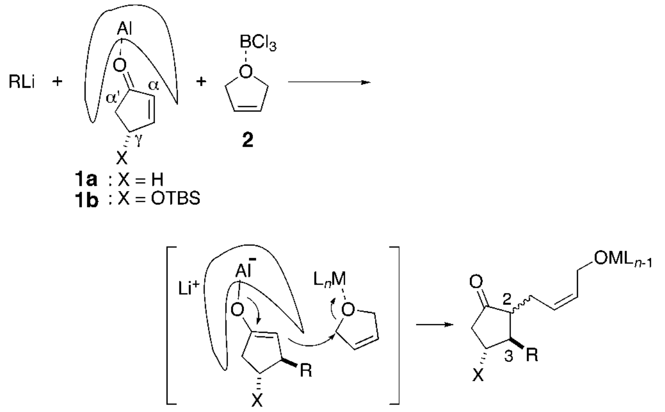
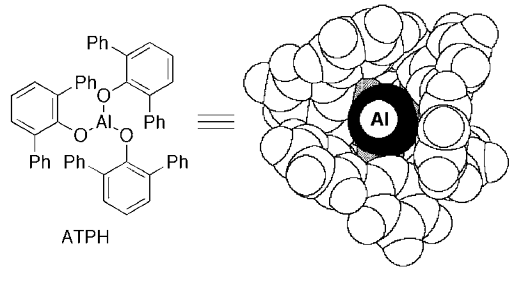
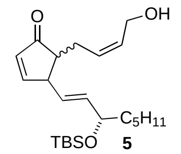
One-pot three-component coupling[1] is an important procedure in organic synthesis and provides a powerful and rapid means for construction of the prostaglandin[2] and jasmonate[3] families. Here we report on a novel strategy for three-component coupling (Scheme 1), which involves the combined use of: 1) an organolithium reagent (RLi); 2) aluminum tris(2,6-diphenylphenoxide) (ATPH;[4] see space-filling model) cyclopentenone complexes **1a** and **1b**; and 3) 2,5-dihydrofuran (DHF)$\cdot$BCl$_3$ complex (**2**). This approach leads efficiently to both *trans*- and *cis*-jasmonate derivatives.



Scheme 1. Three-component coupling using ATPH. TBS = *tert*-butyldimethylsilyl.



Precomplexation of a solution of ATPH (1.05 equiv) in toluene with 2-cyclopenten-1-one (**3a**; 1.0 equiv) at −78 °C was followed by treatment with a solution of isopropenyllithium (1.1 equiv) in DME. After 1 h, sequential addition of DHF (5.0 equiv) and BCl$_3$ (2 equiv) gave three-component coupling product **4**, which was isolated in a yield of 71 % (2,3-*trans*-**4**/2,3-*cis*-**4** = 3.5:1; 2′*E*/2′*Z* = 1:99). The formation of **4** was not observed before treatment with BCl$_3$.[5] The addition of a mixture of DHF and BCl$_3$ gave a yield and selectivity comparable to those achieved by sequential addition. Other alkenyl- and alkynyllithiums, as well as lithium enolates, are well suited to this process and give the corresponding products in moderate to high yields with complete retention of the original *Z* configuration (Table 1). The even more labile cyclopentenone **3b** was also compatible with these basic conditions (entries 3 and 6), but scant 2,3-*cis*/*trans* selectivity was observed with 2-alkylethenyllithiums (entries 2 and 3). The 2,3-*cis* selectivity increases in the order isopropenyl- < crotyl- < alkynyllithium, that is, with decreasing size of the organolithium reagents (each prepared in DME) (entries 1, 2, and 5).[6]



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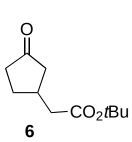

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Tetrahydrofuran was also used as an alkylating agent in place of DHF (Table 2), but in some cases the stereoselectivity was different from that with DHF. For instance, in the case of isopropenyllithium, the 2,3-*cis* product predominated with THF (Table 2, entries 2–4),[6, 7] while the 2,3-*trans* product was formed selectively with DHF (Table 1, entries 4–6). However, both DHF and THF gave the 2,3-*cis* product almost exclusively with 1-hexynyllithium (Table 1, entry 1; Table 2, entry 1).[6, 7] The TBSOTf$\cdot$THF complex gives better 2,3-*cis* selectivity than BCl$_3\cdot$THF (Table 2, entries 2–4). Both THF and DHF showed a general trend to give high 2,3-*trans* selectivity with lithium enolates (Table 1, entries 8 and 9; Table 2, entries 5–7).[8]

With this new method in hand, various *trans*- and *cis*-jasmonate derivatives can be obtained in a few steps by assembling commercially available compounds. For example, stereo- and regioselective methylation of diphenylphosphate **8** (Scheme 2), readily obtained from *trans*-**7**, was effected by using trimethylzincate and a catalytic amount of Fe^{III} (Me$_2$Zn + MeMgBr (2 + 2 equiv); [Fe(acac)$_3$]: 1 mol %)[9] at −78 °C to give *tert*-butyl jasmonate **9** (2,3-*trans*/*cis* > 20:1) together with small amounts of stereo- (2′*Z*/2′*E* = 97:3; **10**, 2 %) and regioisomers (S$_N$2/S$_N$2′ = 87:13; **11**, 11 %); the total yield of isomers was 87 %, and the isomeric purity of **9** was 85 %).[10] The ketone and ester groups remained intact under these conditions. Subsequent displacement of a *tert*-butyl group (HCO$_2$H, RT) led to quantitative formation of *trans*-jasmonic acid.

Likewise, methyl *cis*-jasmonate was easily accessible from three-component coupling product **12** (2,3-*cis*/*trans* = 7.5:1 and 71 % yield from **3a**). After separation of the diastereomers (to 2,3-*cis*/*trans* = 99:1), a similar phosphorylation–methylation[9] sequence (Scheme 3) caused only slight epimerization at C2 and gave **13** (2,3-*cis*/*trans* = 31:1) in a reasonable overall yield together with moderate amounts of stereo-

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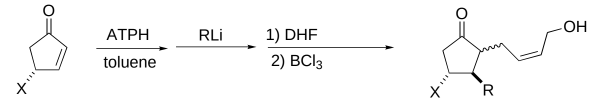
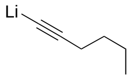
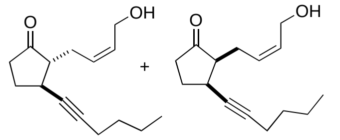
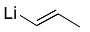
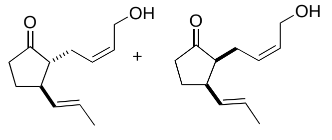
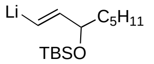
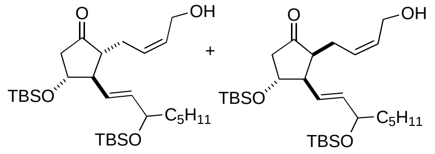
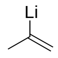
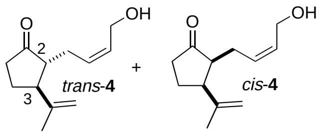
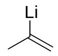
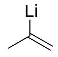
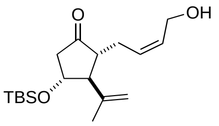
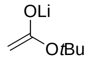
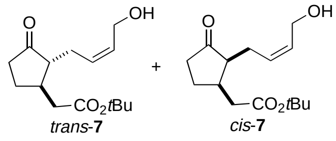
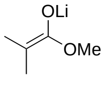
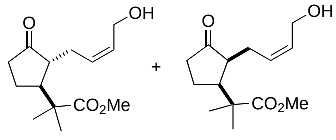
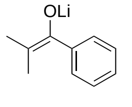
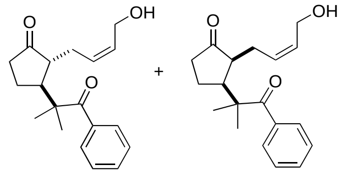
Table 1. Three-component coupling of RLi, **1a** (or **1b**), and DHF · BCl_3 complex.[a]



3a : X = H
3b : X = OTBS

Entry	RLi [equiv][b]	Ketone	Conditions [°C, h][c, d]	Products	Yield [%] (2,3-*trans*/2,3-*cis*)[e]
1	 (1.1)	**3a**	− 78, 2.5; − 40, 2		44 (1:11)
2	 (1.1)	**3a**	− 78, 5; − 40, 0.5		57 (1.2:1)
3	 (1.2)	**3b**	− 78, 20; − 40, 10		46 (1:1)[f]
4	 (1.1)	**3a**	− 78, 17.5; − 40, 3		59 (4.4:1)
5	 (1.1)	**3a**	− 78, 1.5; − 40, 3		71 (3.5:1)
6	 (1.1)	**3b**	− 78, 168		66 (79:11:10)[g]
7	 (2.0)	**3a**	− 78, 18; − 40, 2		69 (>20:1)[h]
8	 (2.0)	**3a**	− 78, 19		47 (>20:1)
9	 (2.0)	**3a**	− 78, 19; − 40, 3		32 (>20:1)

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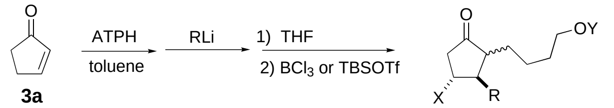
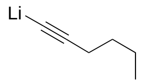
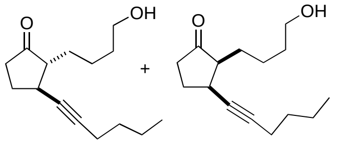
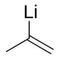
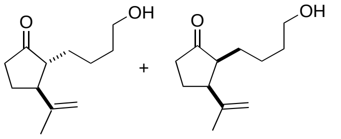
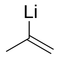
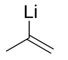
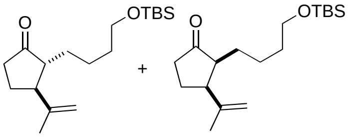
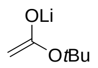
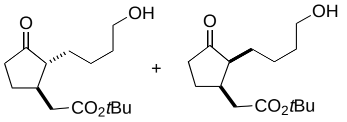
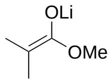
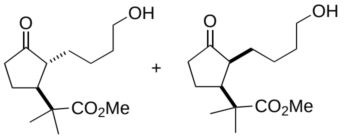
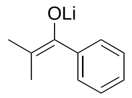
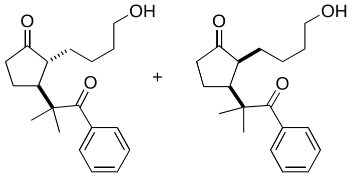
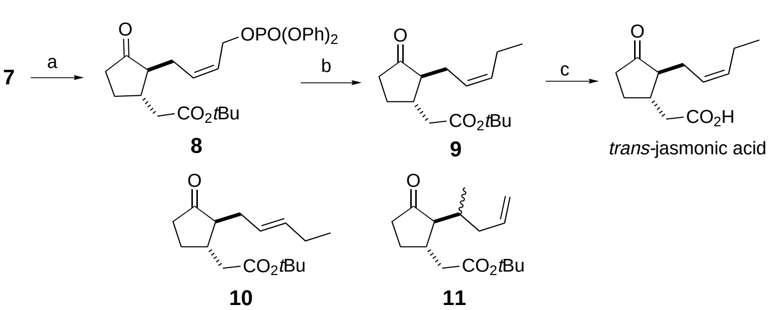
[a] Unless otherwise specified, the reaction was performed with a solution of ATPH (1.05 equiv) in toluene, cyclopentenone (1.0 equiv), organolithium (RLi), BCl_3 or *tert*-butyldimethylsilyl triflate (TBSOTf), and DHF. [b] Each was prepared from the corresponding alkyne, bromide, or tin reagent with BuLi (entries 1 – 6) or from carbonyl compounds and lithium diisopropylamide (LDA; entries 7 – 9) in DME (entries 1 – 3 and 5) or diethyl ether (entries 4 and 6 – 9). [c] The following conditions were used: BCl_3 (2.0 equiv) + DHF (5.0 equiv). [d] The indicated reaction temperatures and times are for the three-component coupling process. [e] Yields of isolated, purified product. The diastereoselectivity was determined by ^1H and ^{13}C NMR spectroscopy. See also ref. [7]. [f] Elimination product **5** (7 %) was also obtained. [g] 2,3-*trans*,3,4-*trans*/2,3-*cis*,3,4-*trans*/2,3-*trans*,3,4-*cis*. [h] Protonated product **6** (27 %) was obtained.

Table 2. Three-component coupling of RLi, ATPH · **3a** (**1a**), and THF · Lewis acid.[a]



Entry	RLi [equiv][b]	Alkylating agent[c]	Conditions [°C, h][d]	Products	Yield [%] (2,3-*trans*/2,3-*cis*)[e]
1	 (1.1)	A	– 78, 2.5; – 40, 2		44 (1: > 20)
2	 (1.1)	A[f]	– 78, 7.5		77 (1:2.7)
3	 (1.1)	A	– 78, 2		85 (1:3.2)
4	 (1.1)	B	– 78, 2; – 40,2.5		74 (1:4.0)
5	 (2.0)	A	– 78, 15		43 (>20:1)
6	 (2.0)	A	– 78, 15		54 (>20:1)
7	 (2.0)	A	– 78, 15		57 (>20:1)

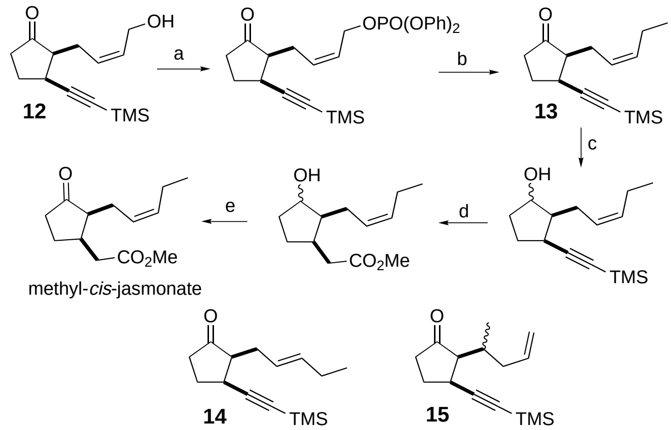
[a] Unless otherwise specified, the reaction was performed with a solution of ATPH (1.05 equiv) in toluene, cyclopentenone (1.0 equiv), organolithium (RLi, THF solution), and BCl_3 or TBSOTf. [b] Each was prepared from the corresponding alkyne, bromide, or tin reagent with BuLi (entries 1–4). Enolates were prepared by using LDA (entries 5–7). [c] The following conditions were used: A) BCl_3 (2.0 equiv) + THF (123 equiv); B) TBSOTf (7.0 equiv) + THF (123 equiv). Organolithiums or enolates were prepared in THF. [d] The indicated reaction temperatures and times are for the three-component coupling process. [e] Yields of isolated, purified products. The diastereoselectivity was determined by ^1H and ^{13}C NMR spectroscopy. See also ref. [7]. [f] BCl_3 (1.1 equiv) was used.



Scheme 2. Synthesis of *trans*-jasmonic acid. Reagents and conditions: a) Et_3N, $ClPO(OPh)_2$, DMAP, CH_2Cl_2, – 20 °C, 90 %; b) $Me_3ZnMgBr$, $[Fe(acac)_3]$ (1 mol %), THF, – 78 °C, < 87 %; c) HCO_2H, RT, > 99 %. DMAP = 4-(dimethylamino)pyridine, acac = acetyl acetone.

($2'Z/2'E = 90{:}10$; **14**, 7 %) and regioisomers ($S_N2/S_N2' = 84{:}16$; **15**, 14 %); the total yield of isomers was 86 %, and the isomeric purity of **13** was 73 %.[10] Reduction of the ketone carbonyl group was followed by hydroboration of the trimethylsilylacetylene[11] and subsequent oxidation. The resulting crude carboxylic acid was selectively methylated, and reoxidation of the remaining hydroxy group would lead to methyl *cis*(*epi*)-jasmonate[12] by the method previously described.[13]

In summary, the present coupling was successful under strongly basic conditions, which is



Scheme 3. Synthesis of methyl *epi*(*cis*)-jasmonate. Reagents and conditions: a) Et_3N, $ClPO(OPh)_2$, −20 °C, 84 %; b) $Me_3ZnMgBr$, $[Fe(acac)_3]$ (5 mol %), THF, −78 °C, <86 %; c) $NaBH_4$, MeOH, 0 °C, 91 % (1,2-*cis*;2,3-*cis*/1,2-*trans*;2,3-*cis* = 3.2:1); d) $(C_6H_{11})_2BH$, THF, 0 °C; H_2O_2, NaOH, MeOH/benzene, 0 °C; $TMSCHN_2$, MeOH, 0 °C, 48 %; e) see ref. [12]. TMS = trimethylsilyl.

otherwise difficult to achieve. The synthetic potential of ATPH may originate from: 1) The effective Michael addition of organolithium reagents due to both steric (prevention of 1,2-addition and α- and/or γ-deprotonation) and electronic (activation of the β-position) influence of ATPH;[4e] and 2) the novel reactivity of the resulting ATPH enolates, which undergo either 2,3-*cis*- or -*trans*-selective alkylation by the DHF/Lewis acid complexes. This eventually accommodated the *Z* geometry of the new double bond in the α chain.

Experimental Section

Representative procedure for the reaction of ATPH · **3a**, isopropenyllithium, and $BCl_3 \cdot$ DHF: **3a** (42 µL, 0.5 mmol) was added to a solution of ATPH (0.53 mmol) in toluene (5.0 mL) at −78 °C under an argon atmosphere. After 20 min, isopropenyllithium [generated by treatment of a solution of isopropenyltributyltin (194 mg, 0.59 mmol) in DME (5.0 mL) with a solution of *n*BuLi (1.66 M, 0.33 mL, 0.55 mmol) in hexane at −78 °C followed by stirring at 0 °C for 12 min and cooling to −78 °C] was transferred by cannula to the solution of ATPH · **3a** at −78 °C. The reaction mixture was stirred at this temperature for 45 min. To this mixture were then added DHF (0.189 mL, 2.5 mmol) and a solution of BCl_3 (1.0 M, 1.0 mL, 1.0 mmol) in hexane. After 1.5 h, the reaction mixture was warmed to −40 °C, stirred for 3 h, quenched with aqueous $NaHCO_3$, filtered through a Celite pad, and extracted with Et_2O. The organic layer was dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel to give **4** (69.4 mg, 71 %) as a pale yellow oil.

trans-**4**: IR (neat): $\tilde{\nu}$ = 3434, 2950, 1734, 1456, 1377, 1148, 1015, 895 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.74–5.63 (m, 1 H), 5.58–5.41 (m, 1 H), 4.87 (dt, 2 H, *J* = 12.3, 1.2 Hz), 4.16 (dd, 2 H, *J* = 6.6, 2.1 Hz), 2.57–2.03 (m, 8 H), 1.76 (s, 3 H), 1.78–1.63 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 219.8, 144.9, 130.5, 128.6, 112.0, 58.0, 52.1, 48.8, 37.8, 26.4, 24.5, 19.0; elemental analysis (%) calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34; found: C, 74.09; H, 9.64. *cis*-**4**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 4.90 (s, 1 H), 4.72 (s, 1 H), 4.18–4.04 (m, 2 H), 2.97–2.90 (m, 1 H), 1.70 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 219.8, 144.2, 130.1, 129.8, 112.4, 58.1, 51.7, 46.4, 36.4, 24.5, 23.4, 22.4.

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[5] This means that neither Li^{I} nor Al^{III} is the activating agent for DHF.

[6] At present, we do not have a reasonable explanation for these unprecedented 2,3-*cis* selectivities, which might be ascribed to steric influence of ATPH.

[7] The diastereoselectivity (2,3-*cis*:2,3-*trans*) of three-component coupling products was determined by ^{1}H and ^{13}C NMR spectroscopy, as well as several *cis* and *trans* equilibration experiments (HCl, MeOH, RT). We found that ^{13}C NMR spectroscopy could be a powerful tool for establishing the relative stereochemistry at the 2,3-vicinal carbon atoms of 2,3-disubstituted-1-cyclopentanones. In general, ^{13}C NMR chemical shifts of C1′ and C1″ of the *cis* adducts appear upfield due to the greater shielding effects compared to those in the *trans* products. For example, *cis*- and *trans*-2,3-dimethylcyclopentanones show δ = 9.5 (2-Me (C1′)) and 14.8 (3-Me (C1″)), and δ = (2-Me (C1′)) and 19.1 (3-Me (C1″)), respectively (J. B. Stothers, C. T. Tan, *Can. J. Chem.* **1974**, *52*, 308); mthyl *epi*-jasmonate, *cis*: δ = 23.0 (2-CH_2 (C1′)), 33.7 (3-CH_2 (C1″)); *trans*: δ = 25.6 (2-CH_2 (C1′)), 37.7 (3-CH_2 (C1″)) (L. Crombie, K. M. Mistry, *J. Chem. Soc. Perkin Trans. 1* **1991**, 1981). We also found that the equilibrium reached an inherent static point depending on the size of the 3-substituent. Thus, the equilibrium lies on the *trans* side in the order of bulkiness: isopropenyl (*cis*:*trans* = 1:25) > crotyl (*cis*:*trans* = 1:11) > 1-hexynyl (*cis*:*trans* = 1:1.6).

[8] In general, the concomitant formation of Michael addition products such as **6** through enolate protonation was a major side reaction. Considerable formation of this type of product (ca. 30 %) was observed in several cases (Table 1, entries 8, and 9; Table 2, entries 1, and 5–7). It is highly unlikely that the *trans* selectivity is due to the work-up procedure, since the same conditions were used throughout the work (see Experimental Section).

[9] The details of this new stereo- and regioselective method for the alkylation of allylic phosphates by the combined use of trialkyl- or tetraalkylzincates and Fe^{III} or Fe^{II} catalysts will be reported elsewhere.

[10] These selectivities (S_N2 vs S_N2'; 2′*E* vs 2′*Z*; 2,3-*cis* vs 2,3-*trans*) were determined by ^{1}H and ^{13}C NMR spectroscopy and GC-MS.

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The First Platinum Formyl, a Member of a Series of Hexanuclear Clusters Exhibiting a Rare Structure**

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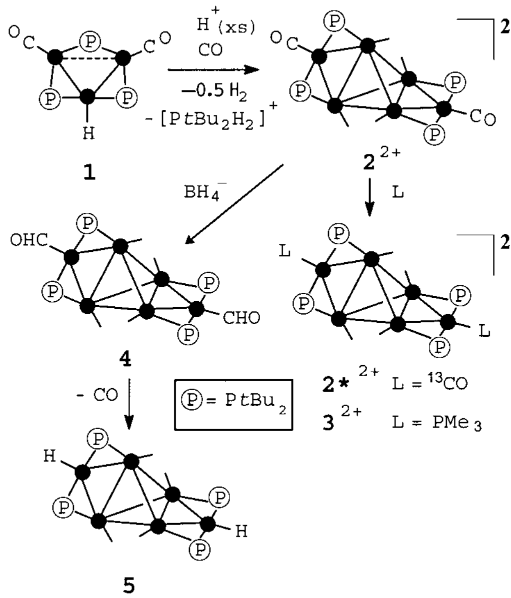
A large number of platinum clusters have been reported in the past decades.[1] Nevertheless, only two hexanuclear structures have been authenticated by X-ray crystallography: the trigonal-prismatic $[Pt_6(\mu\text{-}CO)_6(CO)_6]^{2-}$[2a] and the octahedral $[Pt_6(CO)_6(\mu\text{-}dppm)_3]^{2+}$ (dppm = bis(diphenylphosphanyl)methane).[2b] In addition, the decanuclear $[Fe_4Pt_6(CO)_{22}]^{2-}$,[3] arising from the orthogonal dimerization of two $[Pt_3(CO)_3\{\mu_2\text{-}Fe(CO)_4\}_2]^-$ triangles, contains a tetrahedral Pt core, two opposite edges of which are each bridged by another platinum atom. We have discovered a facile route to platinum clusters having this unusual structure.[4] The precursor $[Pt_6(CO)_6(\mu\text{-}PtBu_2)_4](CF_3SO_3)_2$ (**2**) was prepared by treating the trinuclear hydrido cluster $[Pt_3(H)(CO)_2(\mu\text{-}PtBu_2)_3]$ (**1**)[5] with an excess of triflic acid under a CO atmosphere (Scheme 1).

Figure 1 shows an ORTEP view of the cation $\mathbf{2}^{2+}$, which exhibits overall D_{2d} symmetry.[7] Complex **2** is air-stable, thermally robust (decomp 228 °C), and remains unchanged, even under forcing conditions, in the presence of CO (100 °C, 100 atm, 12 h) or H_2 (80 °C, 90 atm, 6 h). Interestingly, **2** reacts with ^{13}CO to give $[Pt_6(CO)_4(^{13}CO)_2(\mu\text{-}PtBu_2)_4](CF_3SO_3)_2$ (**2***), the product of selective substitution of the carbonyl ligands attached to the two "apical" atoms Pt2 and Pt5. A similar remarkable regioselectivity was also observed in the reactions of **2** with PMe_3 or $NaBH_4$ to give $[Pt_6(CO)_4(PMe_3)_2(\mu\text{-}PtBu_2)_4](CF_3SO_3)_2$ (**3**), and $[Pt_6(CO)_4(CHO)_2(\mu\text{-}PtBu_2)_4]$ (**4**), respectively. The structures of **2***, **3**, and **4** can be clearly assigned on the basis of elemental analyses and IR and NMR spectra. For example, the four bridging P nuclei are still isochronous and in the $^{31}P\{^1H\}$ NMR spectrum they give rise to a central singlet (doublet in **3**, $^2J(P_\mu,P_{term} = 13\ Hz)$ flanked by a complex set of ^{195}Pt satellites, very similar to those observed for **2**. Strong similarities were also observed in the main features of the $^{195}Pt\{^1H\}$ NMR spectra, which still show only two signals and hence rule out all other possible isomers.



Scheme 1. Synthesis and further reactions of **2**.

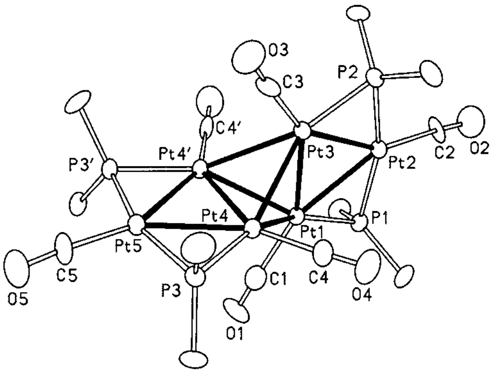


Figure 1. Molecular structure of $\mathbf{2}^{2+}$.[7] Methyl groups are omitted for clarity (thermal ellipsoids at 30% probability; symmetry code: ′ = $x, -y, z$). Selected bond lengths [Å] and angles [°]: Pt1-Pt2 2.758(1), Pt1-Pt3 2.667(1), Pt1-Pt4 2.841(1), Pt2-Pt3 2.762(1), Pt3-Pt4 2.841(1), Pt4-Pt4′ 2.666(1), Pt4-Pt5 2.756(1); Pt3-Pt1-Pt2 61.17(3), Pt1-Pt2-Pt3 57.79(3), Pt1-Pt3-Pt2 61.04(3), Pt3-Pt1-Pt4 62.00 (3), Pt1-Pt3-Pt4 62.00(3), Pt1-Pt4-Pt3 56.00(3), Pt1-Pt4-Pt4′ 62.01(2), Pt3-Pt4-Pt4′ 62.01(2), Pt4′-Pt4-Pt5 61.071(15), Pt4-Pt5-Pt4′ 57.86(3).

Complex **4** is of particular interest, being the first platinum formyl, and its structure was unequivocally confirmed by comparison of its spectra with those of the labeled $[Pt_6(CO)_4(^{13}CHO)_2(\mu\text{-}PtBu_2)_4]$ (**4***). In particular, the triplet for the formyl group at $\delta = 18.9$ ($^3J(H,P) = 14\ Hz$) in the ^1H NMR spectrum of **4** splits as expected in **4*** (brdt, $^1J(C,H) = 152\ Hz$) for coupling with the adjacent ^{13}C nucleus (Figure 2a, b). The same coupling is exhibited by a doublet at $\delta = 244.6$ for the formyl C atom in the proton-coupled ^{13}C NMR spectrum of **4*** (Figure 2c, d).[6a] Furthermore, a

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