[7] J. D. Corbett, *Struct. Bonding (Berlin)* **1997**, *87*, 157, and references therein.
[8] T. A. Albright, J. K. Burdett, M. H.Whangbo, *Orbital Interaction in Chemistry*, Wiley, New York, **1985**.
[9] The spatial drawing of MO obitals was ploted with Molden *v3.3* program. The Molden package was written by G. Schaftenaar, CAOS/CAMM Center Nijmegen, Toernooiveld, Nijmegen, The Netherlands **1997**.
[10] a) Z. Lin, I. D. Williams, *Polyhedron* **1996**, *15*, 3277; b) Z. Lin, M.-F.Fan, *Struct. Bonding (Berlin)* **1997**, *87*, 35; c) Z. Xu, Z. Lin, *Chem. Eur. J.* **1998**, *4*, 28.
[11] a) G. Igel-Mann, H. Stoll, H. Preuss, *Mol. Phys.* **1988**, *65*, 1321; b) D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta* **1990**, *77*, 123; c) W. Kuechle, M. Dolg, H. Stoll, H. Preuss, *Mol. Phys.* **1991**, *74*, 1245.
[12] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1995**.

Two-Step Synthesis of *trans*-2-Arylcyclopropane Carboxylates with 98–100 % *ee* by the Use of a Phosphazene Base

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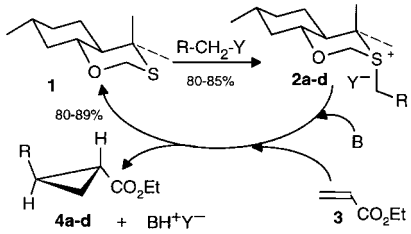
We found recently that oxathiane **1** (see Scheme 1) is a very efficient chiral auxiliary that allows the preparation of various pure *trans*-diarylepoxides in high yields (≈85 %) and with high enantiomeric purities (98.5–99.9 %).[1] We report here the extension of this method to the synthesis of disubstituted cyclopropanes.

Since the first Simmons–Smith reaction in 1958,[2] extensive work has been devoted to the synthesis of enantiomerically enriched polysubstituted cyclopropanes. Pure *trans*- (or pure *cis*-) disubstituted cyclopropanes with levels of enantioselectivity up to 93 % have been obtained from *trans*- (or *cis*-) olefins by the use of stoichiometric quantities of an external chiral promoter and an excess of the preformed $Zn(CH_2I)_2 \cdot$ DME complex.[3] However, with catalytic amounts of a chiral promoter only 90 % *ee* could be achieved.[4] Although styrene was converted into a *trans*-alkoxycarbonyl-substituted cyclopropane with 99 % *ee* by adding only 1 mol % of a chiral copper catalyst,[5] an exotic and very hindered ester had to be used to obtain a *trans*/*cis* ratio of 94/6. Starting from the inexpensive and commercially available ethyl ester, low *trans*/*cis* diastereoselectivities (*trans*/*cis* ≈ 70/30) are obtained. Further difficulties arise from the fact that diazo reagents have to be used and that they have to be added slowly (over about 16 h for 0.02 mol) to avoid the formation of side products.[6, 7] Therefore, for large-scale preparations the sulfur ylide method might be more promising, as already stated by Corey.[8] However, until now the chirality had only been located on the olefinic moiety, and either yields[9] or diastereomeric excesses[10] were low. In the method described here the chirality is located at the sulfur center of the reagent, which is recoverable and can thus be reused (Scheme 1).



Scheme 1. Synthesis of cyclopropanes **4a–d**. **2a**: R = Ph, Y = TfO; **2b**: R = *p*-NCC_6H_4, Y = TfO; **2c**: R = *p*-*t*BuC_6H_4, Y = BF_4; **2c′**: R = *p*-*t*BuC_6H_4, Y = TfO; **2d**: R = 2-naphthyl, Y = BF_4; **4a**: R = Ph; **4b**: R = *p*-NCC_6H_4; **4c**: R = *p*-*t*BuC_6H_4; **4d**: R = 2-naphthyl. B = NaH, Et–P_2.[13]

(Arylmethyl)sulfonium salts **2a–d** were prepared in about 80–85 % yield from RCH_2OH, Tf_2O, and pyridine in CH_2Cl_2[11] or from RCH_2Br $AgBF_4$. Only one diastereomer was detected by ^1H and ^{13}C NMR spectroscopy, and the axial position was assigned for the arylmethyl group in **2b–d** based on a comparison with spectra of the known **2a**.[12] The corresponding ylides were generated in situ with either NaH or $EtN{=}P(NMe_2)_2{-}N{=}P(NMe_2)_3$ ("Et–P_2")[13] as base (Tables 1 and 2). With NaH in THF at −30 °C full conversions were achieved, as seen from the ^1H NMR spectra of the crude product, but 24 to 76 hours were required. Whereas cyclopropane **4a** was isolated in high yield (83 %) and with complete enantioselectivity (100 % *ee*), **4b** and **4d** were obtained with slightly lower enantioselectivities (≈96 % for **4b** and ≈95 % for **4d**, Table 1). Only traces of the *cis* isomer of crude **4d** were detected, but about 15 % of the *cis* isomer was observed for **4b**. Surprisingly, in the case of **4c**, although

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Table 1. Synthesis of cyclopropanes **4a–d** from **2a–d** in THF at −30 °C with NaH as base.

4	R	c_{ylide} [M]	t [h]	Crude product *trans*/*cis*[a]	*trans*-**4** yield [%][b]	*ee* [%][c]	Reisolated **1** [%]
a	C_6H_5	0.22	24	95/5	83	**100**	89
b	*p*-NCC_6H_4	0.23	48	80/20	62	95.8	89
c	*p*-*t*BuC_6H_4	0.23	72	≥99/1	50	60.8	80
d	2-naphthyl	0.19	6	95/5	78	94.8	80

[a] Determined by ^1H NMR spectroscopy (200 MHz). [b] Not optimized. [c] Determined by chromatography on a chiral phase (see ref. [16] and the supporting information).

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the *cis* isomer was not detected, the enantiomeric purity was only 61%.

In an attempt to improve these results and to shorten the reaction time, we decided to generate more reactive "naked" carbanions by using a phosphazene base. Et–P_2 ($pK_a \approx 30$),[14] is potentially able to provide a high concentration of ylide and could be used in CH_2Cl_2. The results are summarized in Table 2. As expected, full conversions were achieved in only

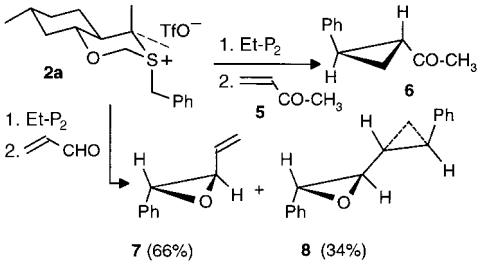
Table 2. Synthesis of cyclopropanes **4a–d** from **2a**,**b**,**c′**,**d** in CH_2Cl_2 with Et–P_2 as base.

4	R	t [min]	T [°C]	c_{ylide} [M]	*trans*/*cis*	*trans*-**4**		Config.
						ee [%][a]	$[\alpha]_D^{24}$ [b]	
a	C_6H_5	15	–30	0.05	95/5	96.7	–232	*R*,*R*
		15	–50	0.25	94/6[a]	97.8		
b	*p*-NCC_6H_4	30	–30	0.05	85/15	99.2	–339	*R*,*R*
		30	–50	0.25	94/6[a]	98.8		
c	*p*-*t*BuC_6H_4	30	–30	0.05	96/4[a]	98.9	–245	*R*,*R*
d	2-naphthyl	30	–30	0.05	93/7	84.4	–215	*R*,*R*
		30	–50	0.25	95/5[a]	94.8		

[a] Determined by gas chromatography on CP-Chirasil-DEX CB and by HPLC on Chiralcel OJ for **4a**, and by HPLC on Chiralcel OJ for **4b–d** (see ref. [16] and the supporting information). [b] In ethanol.

15 to 30 minutes. The percentage of the *cis* isomer for **4b** was reduced to 6%. It is worth noting that in all cases, after chromatographic separation from the starting oxathiane, the *cis* isomers were not detected by ^{1}H NMR spectroscopy (200 MHz). The enantiomeric purities of **4a–c** ranged from 97.8 to 98.9%, and reached 94.8% for **4d**.

The enolizable ketone **5** also reacted smoothly under the same conditions to provide the corresponding cyclopropane **6** in high yield and with high enantioselectivity (98.5% *ee*, Scheme 2). In an analogous manner acrolein led mainly to the



Scheme 2. Reaction of **2a** with acrolein and **5**. The *trans* configuration at the epoxide ring was proven by the coupling constant for the *trans* protons (**7**: $^3J = 2.5$ Hz;[1] **8**: $^3J = 2$ Hz); the configuration at the cyclopropane ring in **8** is unclear.

diastereomerically pure *trans*-epoxide **7** (66%), although the epoxycyclopropane **8** was also observed (34%) as a single diastereomer. The latter was generated by epoxidation of the already formed cyclopropane.

In all the cases the *trans* structure was assigned to the major compound with the help of ^{1}H NMR spectroscopy.[15] The enantiomeric purities were determined by gas chromatography on a CP-Chirasil-DEX CB column in the case of **4a** and **6** or by HPLC on a Chiralcel OJ column in the case of **4a–d**.[16] The 1*R*,2*R* absolute configurations were assigned to *trans*-cyclopropanes **4b–d** and **6** on the basis of the *minus* sign of their optical rotations in ethanol; the 1*R*,2*R* isomer of the known **4a** is levorotatory in ethanol according to Walborsky[17] and Evans.[18] The *R*,*R* absolute configurations (obtained in all cases) are reasonably explained by the model already proposed for the syntheses of mono- and diarylepoxides:[1, 12] The approach of the Michael acceptor occurs opposite to the *gem*-dimethyl group (Figure 1). The very high *ee* values observed (98–100%) could well be due to the participation of the salt present (Et–P_2H^+ TfO^- or BF_4^-) in a coordinative and/or electrostatic interaction in the transition state leading to the cyclization.

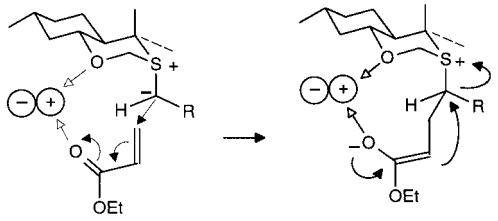


Figure 1. Possible participation of the salt (symbolized by a charge within a circle) in the mechanism of the cyclopropanation.

The chiral sulfur ylide derived from oxathiane **1** provides, in 15 to 30 minutes and with about 90% conversion, 2-arylcyclopropane carboxylates (**4a–d**, **6**) with high enantioselectivities (98–100% *ee*, 95% for **4d**). It is worth noting that these ylides also react smoothly with an enolizable ketone to provide in high yield enantiomerically pure ketocyclopropanes of type **6**, which can then be further derivatized. Although used in stoichiometric amount, the chiral auxiliary is recovered in high yield; we are now searching for a way to avoid the presently necessary chromatographic separation. It is also worth noting that the phosphazene base can be recovered through precipitation of Et–P_2H^+ TfO^-.

Experimental Section

The base (1 equiv) and the Michael acceptor (2 equiv) were successively added (at the desired temperature) to a stirred solution of the sulfonium salt (5 mmol) in anhydrous CH_2Cl_2 (20 mL). The smooth reaction was monitored by thin-layer chromatography (TLC). After the reation was complete, the mixture was poured into cold water, the aqueous phase was extracted with CH_2Cl_2 (5×10 mL), and the organic phases were combined and dried over $NaSO_4$. The cyclopropane derivative and the chiral auxiliary were then separated by chromatography (silica gel, hexane/ether 95/5), and the chiral auxiliary was reused. All compounds gave correct elemental analyses.

2a: ^{1}H NMR (200 MHz, $CDCl_3$, TMS): $\delta = 7.48$ (m, 2H), 7.38 (m, 3H), 5.60 (d, 1H, $^2J = 12$ Hz), 4.80 (d, 1H, $^2J = 12$ Hz), 4.66 (s, 2H), 3.80 (td, 1H, $^3J =$ 10.5, 10.5, 4.5 Hz), 2.01 (m, 1H), 1.80 (m, 2H), 1.74 (s, 3H), 1.68 (s, 3H), 1.50 (m, 2H), 1.30 (q, 1H, $^3J = 11$ Hz), 1.10 (m, 2H), 0.95 (d, 3H, $^3J =$ 6.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$, TMS): $\delta = 130.7$, 71.0 (C), 130.1, 129.8, 127.0, 78.0, 43.0, 31.0 (CH), 58.0, 40.0, 36.0, 33.5, 24.0 (CH_2), 23.5, 22.0, 21.0 (CH_3), 120.7 (q, $J_{CF} = 320$ Hz).

2b: ^{1}H NMR (200 MHz, $CDCl_3$, TMS): $\delta = 7.75$ (AB system, 4H, $^3J =$ 8.5 Hz, $\Delta\nu = 15$ Hz), 5.53 (d, 1H, $^2J = 12$ Hz), 4.96 (d, 1H, $^2J = 12$ Hz), 4.80 (AB system, $^2J = 13$ Hz, $\Delta\nu = 13$ Hz), 3.76 (td, 1H, $^3J = 10.5$, 10.5, 4 Hz), all other signals are very similar to those of **2a**.

2c: ^{1}H NMR (200 MHz, $CDCl_3$, TMS): $\delta = 7.45$ (brs, 4H), 5.62 (d, 1H, $^2J =$ 12 Hz), 4.86 (d, 1H, $^2J = 12$ Hz), 4.57 (s, 2H), 3.80 (td, 1H, $^3J = 10$, 10, 4 Hz), all other signals are similar to those of **2a**. The ^{1}H and ^{13}C NMR

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spectra of **2c′** are identical to those of **2c** with the exception of the signal for the carbon atom of the anion $CF_3SO_2^-$ at $\delta = 120.7$ (q, $J = 320$ Hz).

2d: ^{1}H NMR (200 MHz, CD_2Cl_2, TMS): $\delta = 7.95$ (m, 4H), 7.56 (m, 3H), 5.43 (d, 1H, $^2J = 12$ Hz), 4.90 (d, 1H, $^2J = 12$), 4.77 (AB system, $^2J = 13$ Hz, $\Delta\nu = 15$ Hz), 3.79 (td, 1H, $^3J = 10.5$, 10.5, 4.5 Hz), 2.10 (m, 1H), 1.90 (m, 2H), 1.76 (s, 3H), 1.74 (s, 3H), 1.6 (m, 2H), 1.4 (q, 1H, $J = 11$ Hz), 1.1 (m, 2H), 1.0 (d, 3H, $^3J = 6.5$ Hz); ^{13}C NMR (50 MHz, $CDCl_3$, TMS): $\delta = 134.1$, 133.8, 124.1, 71.5 (C), 131.4, 130.6, 128.5, 128.3, 128.2, 127.7, 127.0, 78.7, 43.7, 31.4 (CH), 58.5, 40.4, 36.9, 34.3, 24.1 (CH_2), 26.2, 22.0, 21.1 (CH_3).

4a: ^{1}H NMR (200 MHz, $CDCl_3$, TMS): $\delta = 7.27$ (m, 3H), 7.13 (m, 2H), 4.18 (q, 2H, $^3J = 7$), 2.53 (ddd, 1H, $J = 9.5$, 6.5, 4 Hz), 1.91 (ddd, 1H, $J = 8.5$, 5.5, 4.5 Hz), 1.61 (ddd, 1H, $J = 9.5$, 5.5, 4.5 Hz), 1.32 (ddd, 1H, $J = 8.5$, 6.5, 4.5 Hz), 1.29 (t, 3H, $^3J = 7$ Hz); ^{13}C NMR (50 MHz, $CDCl_3$, TMS): $\delta =$ 173.5, 140.2 (C), 128.5, 126.5, 126.2, 26.3, 24.2, (CH), 60.7, 17.1 (CH_2), 14.4 (CH_3).

4b: ^{1}H NMR (200 MHz, $CDCl_3$, TMS): $\delta = 7.50$ (d, 2H, $^3J = 8$ Hz), 7.13 (d, 2H, $^3J = 8$ Hz), 4.15 (q, 2H, $^3J = 7$ Hz), 2.49 (ddd, 1H, $J = 10$, 6.5, 4 Hz), 1.91 (ddd, 1H, $J = 8.5$, 5.5, 4 Hz), 1.62 (ddd, 1H, $J = 10$, 5.5, 4.5 Hz), 1.29 (ddd, 1H, $J = 8.5$, 6.5, 4.5 Hz), 1.22 (t, 3H, $^3J = 7$ Hz).

4c: ^{1}H NMR (200 MHz, $CDCl_3$, TMS): $\delta = 7.33$ (d, 2H, $^3J = 8.5$ Hz), 7.06 (d, 2H, $^3J = 8.5$ Hz), 4.16 (q, 2H, $^3J = 7$ Hz), 2.51 (ddd, 1H, $J = 9.5$, 6.5, 4 Hz), 1.90 (ddd, 1H, $J = 8.5$, 5, 4 Hz), 1.60 (ddd, 1H, $J = 9.5$, 5, 4 Hz), 1.34 (ddd, 1H, $J = 8.5$, 6.5, 4 Hz), 1.32 (s, 9H), 1.29 (t, 3H, $^3J = 7$ Hz).

4d: ^{1}H NMR (200 MHz, $CDCl_3$, TMS): $\delta = 7.78$ (m, 3H), 7.57 (s, 1H), 7.45 (m, 2H), 7.21 (dd, 1H, $^3J = 8.5$, $^4J = 2$ Hz), 4.19 (q, 2H, $^3J = 7$ Hz), 2.69 (ddd, 1H, $J = 9.5$, 6.5, 4.5 Hz), 2.01 (ddd, 1H, $J = 8.5$, 5, 4.5 Hz), 1.67 (ddd, 1H, $J = 9.5$, 5, 4.5 Hz), 1.47 (ddd, 1H, $J = 8.5$, 6.5, 4.5 Hz), 1.30 (t, 3H, $^3J =$ 7 Hz); ^{13}C NMR (50 MHz, $CDCl_3$, TMS): $\delta = 173.5$, 137.6, 133.5, 132.4 (C), 128.3, 127.7, 127.5, 126.4, 125.6, 124.9, 124.6, 26.5, 24.3 (CH), 60.9, 17.2 (CH_2), 14.4 (CH_3).

6: ^{1}H NMR (200 MHz, $CDCl_3$, TMS): $\delta = 7.30$ (m, 3H), 7.10 (m, 2H), 2.53 (ddd, 1H, $J = 9$, 6.5, 4 Hz), 2.32 (s, 3H), 2.23 (ddd, 1H, $J = 8$, 5, 4 Hz), 1.70 (ddd, 1H, $J = 9$, 5, 4 Hz), 1.39 (ddd, 1H, $J = 8$, 6.5, 4 Hz); ^{13}C NMR (50 MHz, $CDCl_3$, TMS): $\delta = 207.0$, 140.4 (C), 127.5, 126.5, 126.1, 33.0, 30.9, 29.1 (CH, CH_3), 19.2 (CH_2).

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[1] A. Solladié-Cavallo, A. Diep-Vohuule, V. Sunjic, V. Vinkovic, *Tetrahedron: Asymmetry* **1996**, *7*, 1783.
[2] H. E. Simmons, R. D. Smith, *J. Am. Chem. Soc.* **1958**, *80*, 5323.
[3] A. B. Charette, S. Prescott, C. Brochu, *J. Org. Chem.* **1995**, *60*, 1081.
[4] A. B. Charette, C. Brochu, *J. Am. Chem. Soc.* **1995**, *117*, 11367.
[5] D. A. Evans, K. A. Woerpel, M. M. Hinman, M. M. Faul, *J. Am. Chem. Soc.* **1991**, *113*, 726.
[6] S. E. Denmark, S. P. O'Connor, *J. Org. Chem.* **1997**, 62, 584.
[7] H. Fritschi, U. Leutenegger, A. Pfaltz, *Helv. Chim. Acta* **1988**, *71*, 1553.
[8] E. J. Corey, M. Jautelat, *J. Am. Chem. Soc.* **1967**, *89*, 3912.
[9] M. Calmes, J. Daunis, F. Escale, *Tetrahedron: Asymmetry* **1996**, *7*, 395.
[10] M. J. De Vos, A. Krief, *Tetrahedron Lett.* **1983**, *24*, 103.
[11] a) E. Vedejs, D. A. Engler, *Tetrahedron Lett.* **1976**, 3487; b) E. Vedejs, D. A. Engler, M. J. Mullins, *J. Org. Chem.* **1977**, *42*, 3109.
[12] A. Solladié-Cavallo, A. Adib, M. Schmitt, J. Fischer, A. DeCian; *Tetrahedron: Asymmetry* **1992**, *3*, 1597.
[13] Such phosphazene bases provide very reactive naked anions. One could expect the large Et–P_2H^+ cation to be less tightly associated to its anion and to the ylide, thus allowing an easy access to the ylide. Furthermore, it should be geometrically able to help form the complex of the ylide and the Michael substrate in the transition state.
[14] R. Schwesinger, H. Schlemper, *Angew. Chem.* **1987**, 99, 1212; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1167.
[15] In all cases the CH_2 protons of the ester groups are more shielded (due to the phenyl effect) in the *cis* isomer ($\delta \approx 3.85$, $CDCl_3$) than in the *trans* isomer ($\delta \approx 4.20$, $CDCl_3$). This was already observed for the aldehydic proton in formylphenylcyclopropane: P. Scribe, J. Wiedmann, *Bull. Soc. Chim. Fr.* **1971**, 2268.
[16] The enantiomeric purities were determined by Dr. V. Vinkovic in the group of Prof. V. Sunjic at the Ruder Boskovic Institut of Zagreb.
[17] Y. Inouye, T. Sugita, H. M. Walborsky, *Tetrahedron* **1964**, *20*, 1695.
[18] D. A. Evans, K. A. Woerpel, M. J. Scott, *Angew. Chem.* **1992**, 104, 439; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 430.

Multiple Coordination of Metal Atoms to Arenes: The Coordination of Six Ruthenium Atoms to Naphthalene-1,8-diyl in $[Ru_6(\mu_6\text{-}C_{10}H_6)(\mu_3\text{-}PPh)(CO)_{14}]$**

Antony J. Deeming* and Caroline M. Martin

Research on the incorporation of arenes into clusters has largely been stimulated by their potential as models for chemisorption on metal surfaces and by a wish to modify arene structure and reactivity.[1, 2] The chemistry of benzene with metal clusters has been developed extensively in recent years,[3] and dominant modes of coordination are η^6 coordination at a single metal atom, μ_3-η^2,η^2,η^2 coordination over a triangular cluster face, and combinations of these two modes with σ-M–C bonding, as observed in phenyl and *ortho*-phenylene (1,2-didehydrobenzene) systems. Several of these modes resemble chemisorption of benzene on a (111) metal surface or on step-sites on such surfaces.[4] In contrast, however, relatively few clusters that contain more complex, polycyclic arenes such as naphthalene and anthracene have been reported. Studies of such compounds are often hindered by the difficulty of introducing the polycyclic arene into the coordination sphere of the cluster, and has, so far, centered on mono- and binuclear species, with interactions through either σ bonds, as in $[Fe(C_{10}H_7)_4][LiOEt_2]_2$,[5] or more commonly by π complexation through η^2, η^4, η^6, or bis-allylic η^3:η^3 interactions, as in, for example, the compounds $[Rh_2(C_5Me_5)_2(1,2\text{-}\eta^2\text{-}3,4\text{-}\eta^2\text{-}C_{10}H_8)(PMe_3)_2]$,[6] $[RhCp(\eta^4\text{-}C_{14}H_{10})]$,[7] $[Ru(\eta^4\text{-}C_8H_{12})(\eta^6\text{-}C_{10}H_8)]$,[8] and $[Fe_2(CO)_6(\mu\text{-}\eta^3\text{:}\eta^3\text{-}C_{14}H_{10})]$.[9] One of our recent objectives has therefore been to extend the coordination chemistry of naphthalene and anthracene by the combination of the σ and π M–C interactions that are present in the above molecules, to allow extensive metalation of each ring of the polycyclic arene.

We have introduced polycyclic arenes into the clusters by the thermal degradation of tertiary phosphanes in the presence of metal compounds. The thermolysis of $[Ru_3(CO)_{12}]$

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