The mixture was then cooled to $-78\,^{\circ}C$ and sequentially treated with methyl pyruvate **5** (0.25 mmol) containing methyl-1-naphthoate (internal standard) and ketene thioacetal **4** (0.30 mmol). After transferring the Schlenk tube into an ice bath, samples were taken at time intervals and filtered through a short (2 cm) silica gel plug,[19] and the conversion and the **6**/**7** ratio were determined by GLC.[16] When conversion was complete, the reaction mixture was filtered under an inert atmosphere, and the filtrate containing **6** and **7** was hydrolyzed as described.[16] Yield and *ee* of **7** were determined by ^1H NMR spectroscopy and HPLC (Chiralcel OD-H, 0.5 mL min^{-1}, hexane/2-propanol 99:1), respectively.

The recovered complex $\mathbf{3}\cdot Cu(OTf)_2$ was washed with dry CH_2Cl_2 and dried under vacuum. The MS could be mechanically removed at this stage. Recycle runs were carried out according to the general procedure, beginning with the addition of the initial amount of $Cu(OTf)_2$ (entries 4–8) or skipping this step (entries 9–10).

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[17] Control experiments showed that the enantioselectivities for the formation of **6** and **7** were identical within the experimental uncertainty. Therefore the *ee* values were routinely determined after the conversion of **6** to **7** (see *Experimental Section*).

[18] The heterogeneous nature of the catalytic system was demonstrated by the fact that removing $\mathbf{3}\cdot Cu(OTf)_2$ by filtration at 30 % conversion completely stopped the reaction.

[19] This treatment did not cause desilylation of **6**.

Self-Assembly of Pyramidal Tetrapalladium Complexes with a Halide at the Apex**

Camino Bartolomé, Raquel de Blas, Pablo Espinet,*
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Compared to the ubiquitous presence of μ_1-X and μ_2-X ligands (X = halide), and the frequent μ_3-X coordination (often involved in cubane-like structures), higher coordination numbers for halide ligands in discrete molecules are much less common.[1] A coordination number four (μ_4-X) is rare. Apart from a few scattered cases found in polynuclear V, Mn, Zn, or Sb compounds,[2] the examples known seem to concentrate on d^{10} Cu^I,[3] Ag^I, or Hg^{II} complexes.

The group of Hawthorne[4] has reported a number of such structures based on [12]mercuracarborand-4 macrocycles containing four Hg atoms defining a square plane. These electrophilic Hg atoms can bind one halide in an almost square-planar (for X = Cl) or square-pyramidal (for X = I) fashion, depending on the size of the halide. Removal of the halide guest regenerates the free host. On the other hand, the group of Puddephatt has reported the inclusion of halides in electrophilic bowl-shaped calix(4)arene complexes of Cu^I or Ag^I, where the geometry imposed by the calixarene host can stabilize either μ_3- or μ_4-binding modes of the halide, depending on the size of the latter.[5] The mercury macrocycles cited above, as well as other similar ones containing three or five mercury atoms, can even take a second halide to give bipyramidal structures with one halide at each apex.[6] In all these cases the hosting electrophilic metal centers are d^{10} ions which are involved in a macrocyclic structure which exists independently of the presence of the μ_4-binding halide. We present here a case of self-assembly of d^8 metal centers and halides around a pyramidal halide to give tetrapalladium complexes. Unlike the cases reported by Hawthorne and Puddephat, in our case the metallamacrocycle owes its formation to the halide acting as a template.

The reaction of precursors of "Pd(Fmes)" (Fmes = 2,4,6-tris(trifluoromethyl)phenyl) such as **1** or **2** (Scheme 1)[7] with halides QX (the overall ratio of Pd:X is 4:5) in CH_2Cl_2 affords high yields of the tetrametallic species $Q[Pd_4(Fmes)_4X_5]$ (**3**) (X = Cl, Br, I; Q = PPh_4 or PPN (bis(diphenylphosphane)iminium)).[8] The formation of compounds **3** involves the displacement of MeCN and becomes easier in the order I > Br > Cl; thus, only for X = I is compound **3** readily formed starting from the MeCN-rich complex **2**.

Figure 1 shows the crystal structure of the anion in $(PPN)[Pd_4(Fmes)_4Cl_5]$. The four Pd atoms display a square-

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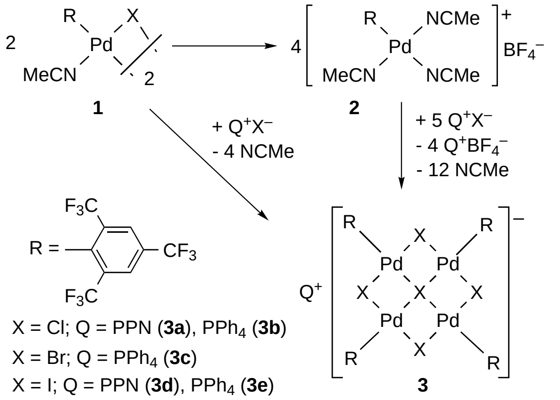


Scheme 1. Synthesis of **3** from **1** or **2**.

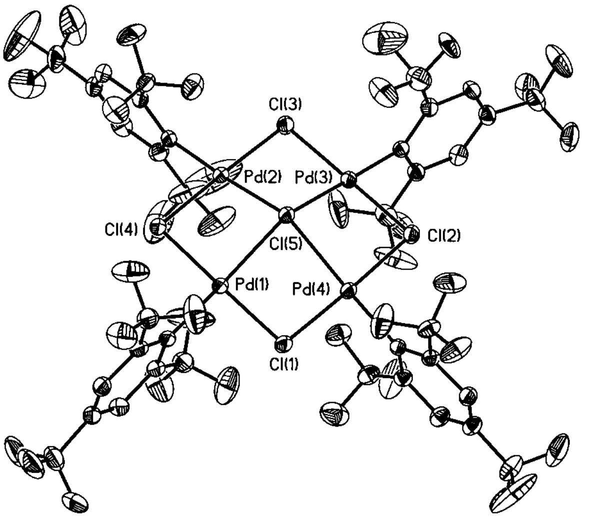
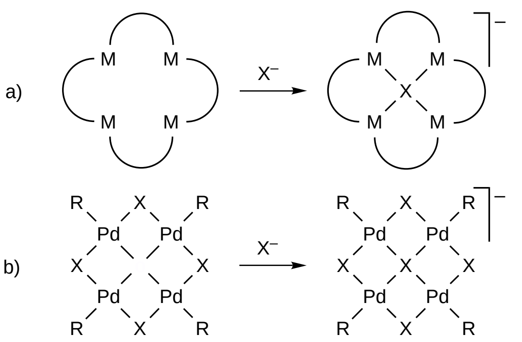


Figure 1. Structure of the anion in the complex (PPN)[$Pd_4(Fmes)_4Cl_5$] (ORTEP view; 30% probability ellipsoids).

planar coordination defined by the *ipso*-C of Fmes, two μ_2-Cl atoms, and the apical μ_4-Cl atom. The latter is located 1.01 Å above the plane defined by the four Pd and the four μ_2-Cl atoms. The μ_4-Cl–Pd distances are 2.56 Å (av), whereas the μ_2-Cl–Pd distances are 2.32 Å (av).[9]

In the systems reported by Hawthorne et al. and Puddephatt et al. (Scheme 2a) the size of the cavity in the metallamacrocycle is independent of the halide to be hosted (although there is some flexibility), whereas in complexes **3** the halide determines both the size of the guest and the cavity (Scheme 2b), and a perfect μ_4-X square-planar coordination with perfectly square-planar-coordinated Pd atoms would require equal bond lengths for μ_2-X–Pd and μ_4-X–Pd. This is not expected since M–X bond lengths increase with an increasing degree of bridging for X.[3, 10] Consequently, the elongation of these bonds forces the central X to be out of the plane defined by the four Pd atoms, the molecule adopting a pyramidal geometry. The preference for pyramidal μ_4-X coordination compared to square-planar μ_4-X has been studied by extended Hückel calculations,[3, 5] and is mostly due to the transformation of a nonbonding orbital in the square-planar geometry (the p_z of X) into a bonding one upon pyramidalization. This leads, in simple terms, to the involvement of three electron pairs of X^- in the formation of four Pd–X bonds, whereas the other two electrons remain as a lone pair on X. Hence these bonds are electron-deficient and long. The less electronegative halogen atoms should, overall, be better donors and atenuate more the intrinsic electron deficiency of the μ_4 bridges. This explains the stability trend observed, I > Br > Cl.



Scheme 2. Incorporation of a halide (X^-) into: a) a metalla-host with a cavity size fixed by the ancillary ligands; b) a hypothetical metalla-host with a cavity size varying with X^- (not implying a real formation pathway).

The complexes display fluxional behavior in solution in noncoordinating solvents which renders equivalent the otherwise diastereotopic internal and external $(CF_3)_{ortho}$ groups. The process has been studied by ^{19}F NMR spectroscopy. The rate of the fluxional process increases in the order Cl > Br > I. Coalescence (at 282.4 MHz for ^{19}F) could be attained only for X = I, Br. Simulation using the gNMR program afforded the activation parameters given in footnote [11]. Although affected by large errors, overall they suggest that the differences in rate in CD_2Cl_2 or $CDCl_3$ for the different complexes are largely associated with entropy, whereas activation enthalpies show only small differences upon changing the halide or the cation, keeping $\Delta H^{\neq}$ at around a value of 38 kJ mol^{-1}.

Different processes that could explain the dynamic behavior observed were considered:

1) Rotation of the Fmes group around the Pd–C bond is excluded by severe steric hindrance.[12]
2) Mechanisms involving Pd–X bond fission (such as apical X^- dissociation–recoordination, or splitting and reforming of one μ_2-bridge, with change of conformation) should be discarded since the differences in Pd–X bond energies should produce noticeably different $\Delta H^{\neq}$ values for the different halides. Moreover, catalytic X^- or slightly coordinating solvents (acetone) should accelerate these processes opening an associative pathway for them, which is not observed. Also, if Pd–X bond fission mechanisms were fast, X exchange in mixtures of complexes **3** with different X ligands should also be fast, and in fact it takes hours in $CDCl_3$ before traces of apparent rearrangement are detected.
3) This leads to inversion of the pyramid as the most likely mechanism.

The inversion of the pyramidal C_{4v} anion implies a D_{4h} transition state with square-planar coordination for the central halide. Density functional thoery (DFT) calculations (B3LYP) of the difference in energy between these two species were made for the model compound $[\mathrm{Pd_4(H)_4Cl_5}]^-$ (Figure 2).[13] A value of 44.1 kJ mol^{-1} was found, which is not in contradiction with the experimental values and suggests that the process is feasible. The transition state implies a considerable shrinkage of the Pd–X bonds to the central halide (from 2.71 to 2.56 Å) and a much smaller stretch of those to the bridging halides (from 2.40 to 2.45 Å). The latter is minimized by opening the Pd-X-Pd angle at μ_2-X (from 88.5 to 95.2°).

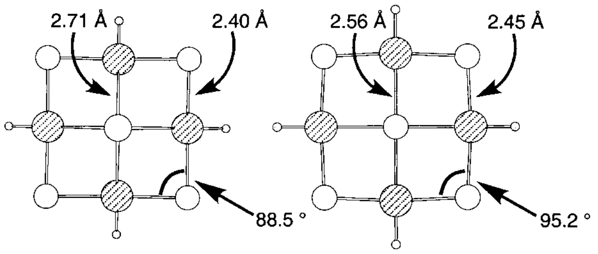


Figure 2. DFT(B3LYP)-optimized structure for the pyramidal fundamental state (left) and the planar transition state (right) of the model compound $[\mathrm{Pd_4(H)_4Cl_5}]^-$.

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[8] All new compounds were fully characterized by elemental analyses and spectroscopic methods. **3a**: Orange crystals; yield 68%; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 298 K): $\delta = 7.70$ (m, 6H; $\mathrm{C_6H_5}$), 7.56 (s, 8H; $\mathrm{C_6H_2(CF_3)_3}$), 7.52 (m, 24H; $\mathrm{C_6H_5}$); ^{19}F NMR (282.4 MHz, $\mathrm{CDCl_3}$, 298 K): $\delta = -57.51$ (s, 24F; *ortho*-$\mathrm{CF_3}$), -63.34 (s, 12F; *para*-$\mathrm{CF_3}$); ^{31}P{^{1}H} NMR (121.4 MHz, $\mathrm{CDCl_3}$, 298 K): $\delta = 21.84$ (s); elemental analysis calcd (%) for $\mathrm{C_{73}H_{40}NCl_7F_{36}P_2Pd_4}$: C 37.30, H 1.72, N 0.6; found: C 37.74, H 1.83, N 0.84. **3b**: Orange crystals; yield 68%; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 298 K): $\delta = 8.00$ (m, 4H; $\mathrm{C_6H_5}$), 7.87 (m, 8H; $\mathrm{C_6H_5}$), 7.73 (m, 8H; $\mathrm{C_6H_5}$), 7.57 (s, 8H; $\mathrm{C_6H_2(CF_3)_3}$); ^{19}F NMR (282.4 MHz, $\mathrm{CDCl_3}$, 298 K): $\delta = -57.45$ (s, 24F; *ortho*-$\mathrm{CF_3}$), -63.36 (s, 12F; *para*-$\mathrm{CF_3}$); ^{31}P{^{1}H} NMR (121.4 MHz, $\mathrm{CDCl_3}$, 298 K): $\delta = 24.15$ (s); elemental analysis calcd (%) for $\mathrm{C_{60}H_{28}F_{36}Cl_5PPd_4}$: C 34.87, H 1.37; found: C 35.73, H 1.73. **3c**: Orange crystals; yield 61%; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 298 K): $\delta = 8.02$ (m, 4H; $\mathrm{C_6H_5}$), 7.88 (m, 8H; $\mathrm{C_6H_5}$), 7.73 (m, 8H; $\mathrm{C_6H_5}$), 7.61 (s, 8H; $\mathrm{C_6H_2(CF_3)_3}$); ^{19}F NMR (282.4 MHz, $\mathrm{CDCl_3}$, 298 K): $\delta = -56.80$ (s, 24F; *ortho*-$\mathrm{CF_3}$), -63.30 (s, 12F; *para*-$\mathrm{CF_3}$); ^{31}P{^{1}H} NMR (121.4 MHz, $\mathrm{CDCl_3}$, 298 K): $\delta = 24.15$ (s); ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_2}$, 298 K): $\delta = 7.92$ (m, 4H; $\mathrm{C_6H_5}$), 7.74 (m, 8H; $\mathrm{C_6H_5}$), 7.64 (s, 8H; $\mathrm{C_6H_2(CF_3)_3}$), 7.60 (m, 8H; $\mathrm{C_6H_5}$); ^{19}F NMR (282.4 MHz, $\mathrm{CD_2Cl_2}$, 298 K): $\delta = -56.56$ (s, 24F; *ortho*-$\mathrm{CF_3}$), -63.11 (s, 12F; *para*-$\mathrm{CF_3}$). ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_2}$, 183 K): $\delta = 7.87$ (m, 4H; $\mathrm{C_6H_5}$), 7.70 (m, 8H; $\mathrm{C_6H_5}$), 7.60 (a, 8H; $\mathrm{C_6H_2(CF_3)_3}$), 7.56 (m, 8H; $\mathrm{C_6H_5}$); ^{19}F NMR (282.4 MHz, $\mathrm{CD_2Cl_2}$, 183 K): $\delta = -56.05$ (s, 12F; *ortho*-$\mathrm{CF_3}$), -57.10 (s, 12F; *ortho*-$\mathrm{CF_3}$), -62.58 (s, 12F; *para*-$\mathrm{CF_3}$); elemental analysis calcd (%) for $\mathrm{C_{60}H_{28}F_{36}Br_5PPd_4}$: C 31.49, H 1.23; found: C 31.62, H 1.28. **3d**: Orange crystals; yield 51%; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 298 K): $\delta = 7.72$ (m, 6H; $\mathrm{C_6H_5}$), 7.65 (s, 8H; $\mathrm{C_6H_2(CF_3)_3}$), 7.53 (m, 24H; $\mathrm{C_6H_5}$); ^{19}F NMR (282.4 MHz, $\mathrm{CDCl_3}$, 298 K): $\delta = -56.47$ (s, 24F; *ortho*-$\mathrm{CF_3}$), -63.21 (s, 12F; *para*-$\mathrm{CF_3}$); ^{31}P{^{1}H} NMR (121.4 MHz, $\mathrm{CDCl_3}$, 298 K): $\delta = 21.8$ (s); ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_2}$, 298 K): $\delta = 7.65$ (m, 6H; $\mathrm{C_6H_5}$), 7.52 (s, 8H; $\mathrm{C_6H_2(CF_3)_3}$), 7.50 (m, 24H; $\mathrm{C_6H_5}$); ^{19}F NMR (282.4 MHz, $\mathrm{CD_2Cl_2}$, 298 K): $\delta = -56.17$ (s, 24F; *ortho*-$\mathrm{CF_3}$), -63.05 (s, 12F; *para*-$\mathrm{CF_3}$); ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_2}$, 203 K): $\delta = 7.62$ (m, 6H; $\mathrm{C_6H_5}$), 7.50 (m, 32H; $\mathrm{C_6H_2(CF_3)_3 + C_6H_5}$); ^{19}F NMR (282.4 MHz, $\mathrm{CD_2Cl_2}$, 203 K): $\delta = -55.67$ (s, 12F; *ortho*-$\mathrm{CF_3}$), -56.90 (s, 12F; *ortho*-$\mathrm{CF_3}$), -62.58 (s, 12F; *para*-$\mathrm{CF_3}$); elemental analysis calcd (%) for $\mathrm{C_{72}H_{38}NF_{36}I_5P_2Pd_4}$: C 31.76, H 1.41, N 0.51; found: C 31.62, H 1.45, N 0.81. **3e**: Orange crystals; yield 66%; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 298 K): $\delta = 8.01$ (m, 4H; $\mathrm{C_6H_5}$), 7.88 (m, 8H; $\mathrm{C_6H_5}$), 7.73 (m, 8H; $\mathrm{C_6H_5}$), 7.66 (s, 8H; $\mathrm{C_6H_2(CF_3)_3}$); ^{19}F NMR (282.4 MHz, $\mathrm{CDCl_3}$, 298 K): $\delta = -56.43$ (s, 24F; *ortho*-$\mathrm{CF_3}$), -63.23 (s, 12F; *para*-$\mathrm{CF_3}$); ^{31}P{^{1}H} NMR (121.4 MHz, $\mathrm{CDCl_3}$, 298 K): $\delta = 24.17$ (s); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 213 K): $\delta = 8.03$ (m, 4H; $\mathrm{C_6H_5}$), 7.90 (m, 8H; $\mathrm{C_6H_5}$), 7.70 (m, 16H; $\mathrm{C_6H_5 + C_6H_2(CF_3)_3}$); ^{19}F NMR (300 MHz, $\mathrm{CDCl_3}$, 213 K): $\delta = -56.03$ (s, 12F; *ortho*-$\mathrm{CF_3}$), -56.98 (s, 12F; *ortho*-$\mathrm{CF_3}$), -62.81 (s, 12F; *para*-$\mathrm{CF_3}$); ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_2}$, 298 K): $\delta = 7.90$ (m, 4H; $\mathrm{C_6H_5}$), 7.75 (m, 8H; $\mathrm{C_6H_5}$), 7.70 (s, 8H; $\mathrm{C_6H_2(CF_3)_3}$), 7.60 (m, 8H; $\mathrm{C_6H_5}$); ^{19}F NMR (282.4 MHz, $\mathrm{CD_2Cl_2}$, 298 K): $\delta = -56.16$ (s, 24F; *ortho*-$\mathrm{CF_3}$), -63.05 (s, 12F; *para*-$\mathrm{CF_3}$); ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_2}$, 193 K): $\delta = 7.88$ (m, 4H; $\mathrm{C_6H_5}$), 7.65 (m, 24H; $\mathrm{C_6H_5 + C_6H_2(CF_3)_3}$); ^{19}F NMR (282.4 MHz, $\mathrm{CD_2Cl_2}$, 193 K): $\delta = -55.65$ (s, 12F; *ortho*-$\mathrm{CF_3}$), -56.90 (s, 12F; *ortho*-$\mathrm{CF_3}$), -62.57 (s, 12F; *para*-$\mathrm{CF_3}$); elemental analysis calcd (%) for $\mathrm{C_{60}H_{28}F_{36}I_5PPd_4}$: C 28.55, H 1.12; found: C 28.52, H 1.10.

[9] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-157188 (**3a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[11] gNMR version 3.6, P. H. M. Budzelaar, IvorySoft, **1996**. **3c** in $\mathrm{CD_2Cl_2}$: $\Delta H^{+} = 37.5 \pm 1.9$ kJ mol^{-1}, $\Delta S^{+} = -7 \pm 9$ J mol^{-1} K^{-1}, $\Delta G^{\ddagger}_{\mathrm{coal}} = 39 \pm 3$ kJ mol^{-1} at 207 K, $\Delta G^{\ddagger}_{273} = 39 \pm 3$ kJ mol^{-1}; **3e** in $\mathrm{CD_2Cl_2}$: $\Delta H^{+} = 39 \pm 2$ kJ mol^{-1}, $\Delta S^{+} = -31 \pm 10$ J mol^{-1} K^{-1}, $\Delta G^{\ddagger}_{\mathrm{coal}} = 47 \pm 3$ kJ mol^{-1} at 248 K, $\Delta G^{\ddagger}_{273} = 47 \pm 3$ kJ mol^{-1}; **3d** in $\mathrm{CD_2Cl_2}$: same values as the previous; **3e** in $\mathrm{CDCl_3}$: $\Delta H^{+} = 36 \pm 4$ kJ mol^{-1}, $\Delta S^{+} = -44 \pm 15$ J mol^{-1} K^{-1}, $\Delta G^{\ddagger}_{\mathrm{coal}} = 47 \pm 5$ kJ mol^{-1} at 241 K, $\Delta G^{\ddagger}_{273} = 48 \pm 6$ kJ mol^{-1}.

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[13] The calculations were carried out with the Gaussian 98 suite of programs: Gaussian 98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**. Pd was represented with the Hay-Wadt relativistic core potential (ECP) for the 28 innermost electrons and its associated double-ζ basis set.[14] Cl was also described with the Los Alamos ECPs and their associated double-ζ basis set augmented by a d polarization function.[15, 16] A 6–31G(d,p) basis set was used for H atoms.[17] Full optimizations without symmetry constraints have been carried out at the B3LYP level.[18, 19]

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Tin-Free Radical Acylation Reactions with Methanesulfonyl Oxime Ether**

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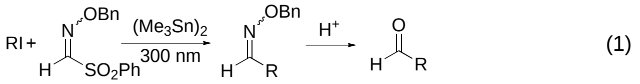
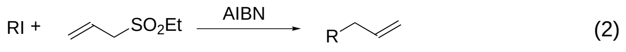
Recent advances in radical reactions have greatly benefited from the efficiency of organotin reagents as mediators. However, organotin reagents are highly toxic, and it is difficult to remove their residues from the products. These disadvantages have proved to be a serious barrier to industrial applications. To solve the problems associated with toxic organotin reagents, several alternative approaches, including the use of polymer-supported organotin reagents and organosilanes, have been utilized with some success.[1] Recently, a few tin-free carbon–carbon bond-forming reactions were reported; they include organosulfone-mediated radical allylation, alkenylation, alkynylation, and azidation reactions.[2–4]

Recently, we reported highly efficient tin-mediated radical acylation reactions with sulfonyl oxime ethers [Eq. (1)].[5] We then studied the possibility of environmentally benign tin-free radical acylation reactions. Our approach is largely based on the tin-free radical allylation reaction of Zard et al. [Eq. (2)][2]

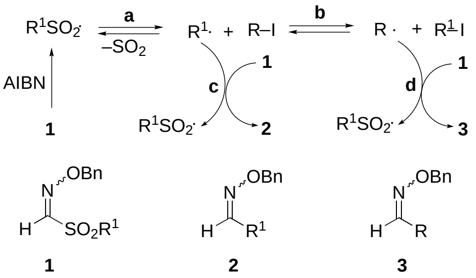


(1)



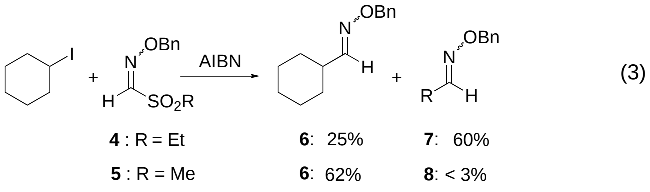
(2)

and involves thermal decomposition of an alkylsulfonyl radical (path a) and subsequent transfer of an iodine atom (path b),[6] as outlined in Scheme 1. The problem with tin-free radical acylation arises from the fast addition of an alkyl radical to sulfonyl oxime ether **1** to afford oxime ether **2**.[7] Since the direct addition of the alkyl radical to sulfonyl oxime ether **1** (path c) would compete with transfer of an iodine atom (path b) in the radical acylation approach, efficient iodine transfer is a key factor for the success of this approach.



Scheme 1. Pathways for the radical reaction of an alkyl iodide with **1**.

We first studied the efficiency of iodine-atom transfer from a secondary alkyl iodide to an ethyl radical relative to the addition of the ethyl radical to ethanesulfonyl oxime ether **4** [Eq. (3)]. Treatment of cyclohexyl iodide with an equimolar amount of **4** and azobisisobutyronitrile (AIBN; 0.1 equiv) in refluxing heptane for 24 h resulted in a 25:60 mixture of two oxime ethers **6** and **7**. Evidently, addition of the ethyl radical to **4** is more than two times faster than the transfer of the iodine atom from cyclohexyl iodide to the ethyl radical. Although the yield of **6** was increased to 48% along with 21% of **7** by using a large excess of cyclohexyl iodide (5 equiv), the serious problem of the formation of **7** could not be solved, and this indicates that **4** is not suitable for tin-free radical acylation with secondary alkyl iodides.



(3)

We next turned our attention to methanesulfonyl oxime ether **5**. Although it was reported that the methanesulfonyl

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