

Transition Metal–Organoindium Chemistry. Addition of Alkyl–Indium Bonds to Alkyliridium Compounds and the Structure of IrH(Et)(Et₂In)(PMe₃)₃

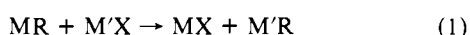
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Abstract: Alkyl–indium bonds of bromodimethylindium, trimethylindium, and triethylindium add to the iridium compound IrMe(PMe₃)₄, and the products IrMe₂(InMeBr)(PMe₃)₃ (1,2), IrMe₂(InMe₂)(PMe₃)₃ (3,4), and IrH(C₂H₅)(In(C₂H₅)₂)(PMe₃)₃ (5) have been isolated and characterized. The addition reaction of trimethylindium is reversed by exposure to excess trimethylphosphine or ethylene. For the triethylindium–hydridoiridium compound 5 an X-ray structure determination has been completed: space group *P*2₁/*n*; *a* = 14.836 (3), *b* = 14.658 (3), *c* = 11.022 (2) Å; β = 90.22 (1)°; *Z* = 4. An uncommon 3-coordinate organoindium entity is present in this compound. Dimethylzinc and IrMe(PMe₃)₄ react analogously; reactions between alkylplatinum and alkylrhodium compounds and alkylindium compounds have been observed, but products have not been isolated.

Volatile organometallic compounds of the main-group metals have become profoundly important in the growth and processing of semiconductor devices. Critical to this application of alkylmetal compounds are reactions that cleave the metal–alkyl bond, removing the organic ligands from the metal atom and allowing it to assume its position on the growing surface of the desired material.¹ We became interested in whether a transition-metal center could participate—ideally, catalytically—in some reaction(s) leading to main-group metal–alkyl bond cleavage at much lower temperatures.

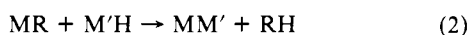
At first glance, there are countless reactions wherein a transition-metal center brings about main-group metal–alkyl bond cleavage, but nearly all are alkyl/halide or alkyl/(alk)oxide exchange, as in eq 1. As a potential source of main-group metal



X = halogen, M = main-group metal compound, R = alkyl, M' = transition-metal compound

atoms, this reaction is self-defeating, since the halo/alkoxide groups are more difficult to remove from the main-group metal atom than are alkyl groups.

A more promising reaction is bimolecular elimination; in one manifestation of this reaction type an active hydrogen atom participates in the elimination of alkane (eq 2).^{2a} (In the case



R = alkyl, M = main-group metal compound, M' = transition-metal compound

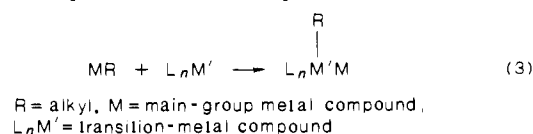
when M' is another main-group atom, e.g. Si, P, As, S, instead of a transition-metal center, this reaction is extremely important in the growth of semiconductor devices, mentioned earlier.^{1,3,4)}

(1) The literature on this topic is vast. See, for instance: Stringfellow, G. B.; Buchan, N. I.; Larsen, C. A. In *Materials Research Society Symposia Proceedings*; Hull, R., Gibson, J. M., Smith, D. A., Eds.; Materials Research Society: Pittsburgh, PA, 1987; Vol. 94, pp 245–253, and other articles in this volume.

(2) (a) Tuck, D. G. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1982; Vol. 1, Chapter 7, pp 683–723. Boocock, S. K.; Shore, S. B. *Ibid.*; Vol. 6, Chapter 41.2, pp 947–981. (b) Clarkson, L. M.; Clegg, W.; Norman, N. C.; Tucker, A. J.; Webster, P. M. *Inorg. Chem.* **1988**, *27*, 2653–2660.

(3) See: Pitt, C. G.; Purdy, A. P.; Higa, K. T.; Wells, R. L. *Organometallics* **1986**, *5*, 1266–1268 and references therein. See also: Cowley, A. H.; Benac, B. L.; Ekerdt, J. G.; Jones, R. A.; Kidd, K. B.; Lee, J. Y.; Miller, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 6248–6249. A novel MM' compound prepared, however, by customary nucleophilic reagents is described by: Byrne, E. K.; Parkanyi, L.; Theopold, K. H. *Science* **1988**, *241*, 332–334.

Another promising reaction type is direct bimolecular addition, summarized in eq 3. Literature examples of this third reaction



include the addition of alkyltin⁵ or -lead^{5,6} compounds to platinum centers and addition of alkylmercury^{7,8} and the postulated addition of alkylcadmium⁸ compounds to certain other metal centers. In the course of our studies we discovered additional remarkable examples of this reaction type, leading to a family of compounds described herein.

Our particular interest was in alkylindium chemistry and we hoped to find some transition-metal compound(s) that could cleave alkyl–indium bonds, at the same time avoiding the conventional reactions summarized in eq 1 and 2. This required transition-metal compound(s) having no halides or alkoxides and no acidic hydrido hydrogen atoms.^{2a} We decided to work with electron-rich transition-metal compounds capable (at least in principle) of forming Lewis acid–base adducts with organoindium compounds, reminiscent of the alkylaluminum adducts studied by Mayer and Calabrese in this department.⁹ From earlier work we were familiar with several methyl(trimethylphosphine)iridium compounds that are quite reactive toward a variety of organic substrates,¹⁰ and which might form adducts with organoindium compounds. We soon found that reactions between methyl(tri-

(4) Interestingly, conditions that suppress (rather than enhance) this reaction can be advantageous. Moss, R. H.; Evans, J. S. *J. Cryst. Growth* **1981**, *55*, 129–134.

(5) Eaborn, C.; Pidcock, A.; Steele, B. R. *J. Chem. Soc., Dalton Trans.* **1976**, 767–776 and references therein. Eaborn, C.; Kundu, K.; Pidcock, A. *Ibid.* **1981**, 1223–1232. Al-Allaf, T. A. K.; Eaborn, C.; Kundu, K.; Pidcock, A. *J. Chem. Soc., Chem. Commun.* **1981**, 55–56. Al-Allaf, T. A. K.; Butler, G.; Eaborn, C.; Pidcock, A. *J. Organomet. Chem.* **1980**, *188*, 335–343.

(6) Jawad, J. K.; Puddephatt, R. *J. Inorg. Chim. Acta* **1978**, *31*, L391–L392.

(7) One remarkable example of R₂Hg addition was reported by: Clark, G. R.; Hoskins, S. V.; Roper, W. R. *J. Organomet. Chem.* **1982**, *234*, C9–C12.

(8) Razuvaev, G. A.; Lityaeva, V. N.; Vishinskaya, L. I.; Cherkasov, V. K.; Korneva, S. P.; Spiridonova, N. N. *J. Organomet. Chem.* **1977**, *129*, 169–174. Use of R₂Cd, R₂Hg addition in syntheses of novel transition-metal compounds is described by: Roper, W. R. *Ibid.* **1986**, *300*, 167–190.

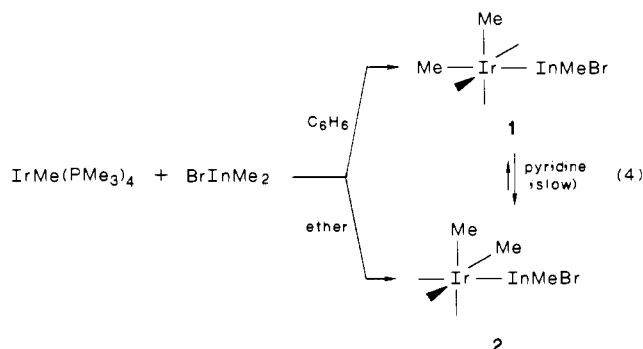
(9) Mayer, J. M.; Calabrese, J. C. *Organometallics* **1984**, *3*, 1292–1298 and references therein.

(10) (a) Thorn, D. L. *Organometallics* **1982**, *1*, 197–204; *J. Mol. Catal.* **1982**, *17*, 279–288. (b) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984–5986. (c) Calabrese, J. C.; Colton, M. C.; Herskovitz, T.; Klambunde, U.; Parshall, G. W.; Thorn, D. L.; Tulip, T. H. *Anr. N.Y. Acad. Sci.* **1983**, *415*, 302–313. (d) Tulip, T. H.; Thorn, D. L., unpublished work. (e) Thorn, D. L. *Organometallics* **1986**, *5*, 1897–1903.

methylphosphine)iridium(I) and alkylindium compounds do occur, rapidly and reasonably cleanly under appropriate conditions, but the reactions involve actual alkyl-indium bond cleavage instead of Lewis acid-base adduct formation.

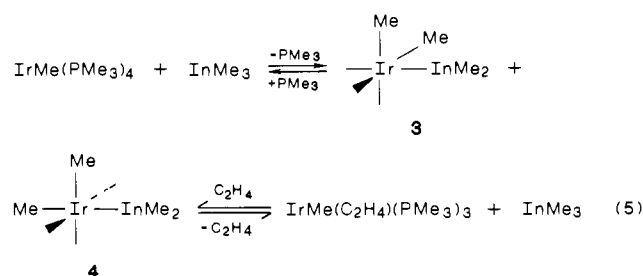
Results

The first reactions attempted were between BrInMe_2 and MeIr(I) substrates. In tetrahydrofuran solution at room temperature the reaction between BrInMe_2 and $\text{IrMe(PMe}_3)_4$ forms a mixture of two products, characterized as the *mer* and *fac* isomers of $\text{Ir(Me)}_2(\text{InMeBr})(\text{PMe}_3)_3$ (compounds **1,2**; eq 4).



Reasonably pure samples of the separate isomers can be obtained by using different solvents. When the reagents are combined in benzene, *mer* compound **1** precipitates. Redissolved in pyridine, its initial NMR spectrum is quite unambiguous for a compound having two inequivalent IrCH_3 groups and one InCH_3 group. But on standing in pyridine solution compound **1** slowly isomerizes to the *fac* isomer **2**, with two chemically equivalent IrCH_3 groups. Combining $\text{Ir(CH}_3)(\text{PMe}_3)_4$ and BrInMe_2 in ether causes *fac* compound **2** to precipitate, and in pyridine solution **2** slowly isomerizes to the same mixture of *mer* and *fac* compounds. Evidently an equilibrium is established between *mer* and *fac* compounds, favoring the *fac* isomer in solution at room temperature.

Upon finding that (trimethylphosphine)methyliridium(I) compounds add the In-CH_3 bond of BrInMe_2 in preference to the In-Br bond, we tried the reactions of MeIr(I) compounds with InMe_3 . In benzene or alkane solution both $\text{IrMe(PMe}_3)_4$ and $\text{IrMe(C}_2\text{H}_4)(\text{PMe}_3)_3$ react rapidly with InMe_3 -ether to form mixtures of *fac*- and *mer*- $\text{IrMe}_2(\text{InMe}_2)(\text{PMe}_3)_3$, compounds **3** and **4** (eq 5), in essentially quantitative in situ yield. After drying in vacuo (to remove ether, PMe_3 , and any excess InMe_3) the material can be recrystallized, with poor recovery, from warm pentane solution. Both the crude reaction mixtures and the recrystallized material consist primarily of the *fac* isomer **3** with ca. 15% of the *mer* isomer **4**. Distinct NMR signals are seen for all methyl groups of both isomers, except for the InMe_2 groups, which display only a single peak (somewhat broad) at room temperature. The position of this peak varies from sample to sample, probably owing to rapid In/Me exchange among compounds **3** and **4** and traces of excess InMe_3 . The *fac-mer* mixture apparently comprises an equilibrium mixture, like the BrInMe_2 adducts **1** and **2**. Ethylene reversibly displaces InMe_3 from compounds **3** and **4**, establishing an equilibrium with the compound $\text{Ir(Me)(C}_2\text{H}_4)(\text{PMe}_3)_3$ (eq 5). Reversible loss of InMe_3



from compounds **3** and **4** also allows $^{13}\text{CH}_3$ scrambling between iridium and indium: $\text{Ir}(^{13}\text{CH}_3)(\text{PMe}_3)_4$ and $\text{In}(^{12}\text{CH}_3)_3$ react to

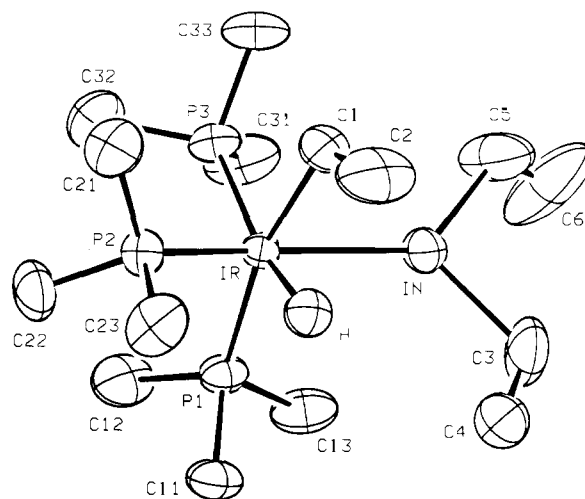
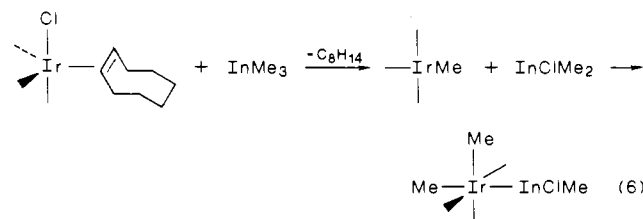


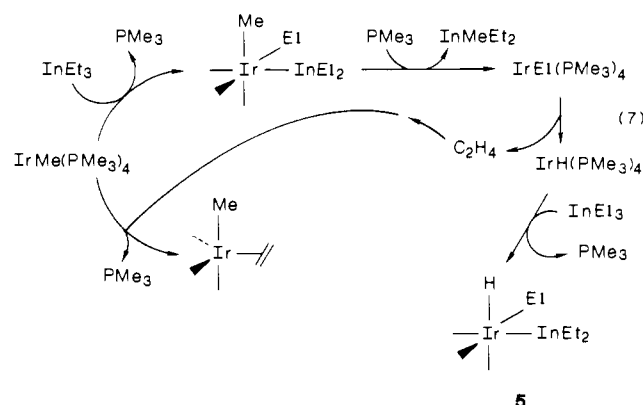
Figure 1. Perspective drawing of $\text{IrH(Et)(Et}_2\text{In)(PMe}_3)_3$. Thermal ellipsoids are drawn at the 50% probability level.

form compounds **3** and **4** with a completely statistically scrambled $^{13}\text{CH}_3$ population. While the remaining InCH_3 groups of compounds **3** and **4** may be exchanging on the NMR time scale, they are unreactive toward methyliridium(I), and mixtures of **3** and **4** with either $\text{IrMe(PMe}_3)_4$ or $\text{IrMe(C}_2\text{H}_4)(\text{PMe}_3)_3$ are stable for several days at room temperature.

Other organoiridium(I) compounds react with InMe_3 but form complex mixtures of products that have not been completely characterized. For instance, the reaction between $\text{IrH(PMe}_3)_4$ and InMe_3 results in several compounds, some containing IrH and IrCH_3 groups (NMR). Likewise, $\text{Ir}(p\text{-MeC}_6\text{H}_4)(\text{PMe}_3)_3$ forms several products with InMe_3 , some containing IrCH_3 groups. Alkyl/aryl redistribution reactions may be occurring. $\text{IrCl(C}_8\text{H}_{14})(\text{PMe}_3)_3$ ¹¹ and InMe_3 react in benzene to form a *mer*- IrMe_2 compound, most likely the chloro analogue of **1** formed in a chloro/methyl redistribution sequence (eq 6).



InEt_3 is also quite reactive toward the iridium compounds used in this study. InEt_3 and $\text{Ir(Me)(PMe}_3)_4$ react rapidly to form a mixture of several compounds, the most readily identifiable being ethylene and $\text{Ir(Me)(C}_2\text{H}_4)(\text{PMe}_3)_3$. Two hydridoiridium compounds are present, $\text{IrH(PMe}_3)_4$ and a new compound, which we have identified as $\text{IrH(C}_2\text{H}_5)(\text{In(C}_2\text{H}_5)_2)(\text{PMe}_3)_3$ (**5**) (see below). A scheme to account for these products is presented in eq 7. In



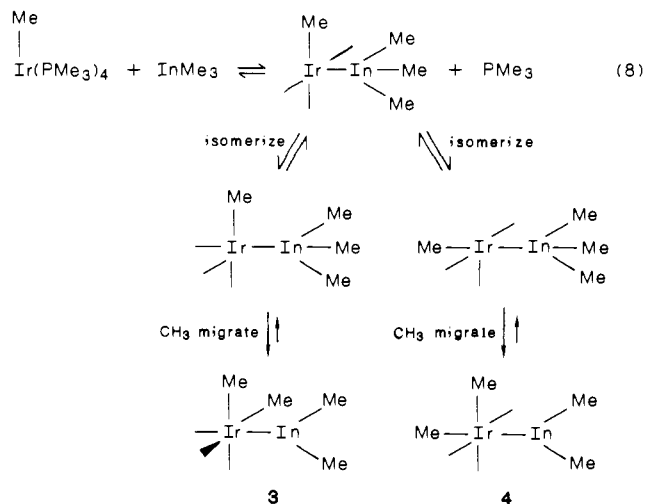
this scheme, compound **5** arises from a reaction between InEt_3 and $\text{IrH}(\text{PMe}_3)_4$. Separate experiments verified this reaction and provided single crystals of compound **5**, used for the X-ray structure determination (see Figure 1).

Discussion

Our initial expectation was that reactions involving the In–alkyl bond would be most easily detected via the observation of alkyl exchange between indium and the transition-metal substrate (case A or B of ref 6). This proved to be wrong, and the oxidative addition of the In–alkyl bond to iridium(I) compounds was immediately revealed in the reaction between BrInMe_2 and $\text{IrMe}(\text{PMe}_3)_4$ (eq 4). Given that the Br–In bond of BrInMe_2 is readily ionized, we had expected an oxidative or ionic addition of $(\text{Br}^-)(\text{InMe}_2^+)^{12}$ to Ir(I). While this may happen at intermediate stages of the reaction, in the observed products it is only the In–alkyl bond that has been added to Ir(I). The propensity of transition-metal compounds to add a main-group metal–alkyl or –aryl bond in preference to a main-group metal–halo bond is already established for reactions between mixed organohalotin and -lead compounds and certain Pt(0) and Pt(II) compounds.⁵ But certain other Pt(0) and Pt(II) compounds do add the halo-metal bond of alkylhalosilicon, -germanium, -tin, and -lead compounds.¹³ These addition reactions are probably controlled by a delicate thermodynamic balance of energies of metal–alkyl and metal–halo compounds; it is unlikely that there are kinetic constraints in the iridium system, given the lability of the InMe_3 adducts and the interconvertibility of *mer* and *fac* isomers **1** and **2**.

Realizing that In– CH_3 bonds are thermodynamically favored to add to Ir(I), we naturally devoted most of our effort to studying the reaction chemistry of trialkylindium compounds. The most straightforward reaction of InMe_3 is with $\text{IrMe}(\text{PMe}_3)_4$, which makes an equilibrium mixture of *fac*- and *mer*- $\text{IrMe}_2(\text{InMe}_2)(\text{PMe}_3)_3$ isomers **3** and **4** (eq 5). This addition is reversible, and InMe_3 can be displaced from **3** and **4** by adding PMe_3 . Likewise, excess ethylene reversibly displaces InMe_3 from **3** and **4** to form $\text{IrMe}(\text{C}_2\text{H}_4)(\text{PMe}_3)_3$; in an open reaction vessel under an inert atmosphere ethylene is released, and the mixture of compounds **3** and **4** is reestablished. A complication is that InMe_3 forms adducts with any Lewis base, including PMe_3 and diethyl ether, and the presence of these Lewis bases can shift the equilibrium between compounds **3** and **4** and InMe_3 -base. In fact we were initially at pains to prepare InMe_3 free from ether, and $\text{IrMe}(\text{olefin})(\text{PMe}_3)_3$ compounds free from labile phosphine, in order to prevent competition by Lewis base adduct chemistry of InMe_3 . But these precautions proved unnecessary as equilibrium positions favor the iridium–alkylindium products and competing phosphine or ether is easily removed.

While the exact mechanism of the In– CH_3 bond addition has not been established, an extremely plausible scheme is shown in eq 8. Here, the initial step is InMe_3 coordination to the basic, electron-rich $\text{MeIr}(\text{I})$ species, forming an adduct familiar from the work of Mayer and Calabrese.⁹ Following (or in concert with) rearrangement of the phosphine ligands, a methyl group migrates from the indium atom to the iridium atom, where the indium center mimics a carbon center in the reverse of the well-known alkyl \rightarrow alkylidene/carbene migration reaction.^{10b,c,14} If these steps are general and reversible, the chemistry observed in this study can be accounted for.



The reaction between InMe_3 and other iridium substrates is much less straightforward. $\text{IrH}(\text{PMe}_3)_4$ and InMe_3 react rapidly, forming a complicated mixture of several products. The ^1H NMR spectrum contains resonances of new hydrido and methyl compounds, possibly including $\text{IrH}(\text{Me})(\text{InMe}_2)(\text{PMe}_3)_3$ (analogous to compounds **3** and **4**), but positive identification has not been made. Fortunately, the reaction between InEt_3 and $\text{IrH}(\text{PMe}_3)_4$ is considerably cleaner (see below).

Adding an In– CH_3 bond to a transition-metal complex, especially a transition-metal complex that binds methyl groups even more strongly than does indium, does not necessarily “activate” the indium entity toward further reaction. There is no a priori reason that alkyl groups are more easily removed from **3** and **4** than from InMe_3 itself. Our hope was to identify new reactions that do remove indium or iridium methyl groups from **3** and **4**, but here we have had no great success: All reactions we tried with compounds **3** and **4** (e.g. hydrogenolysis, aldehyde addition, alkyl halide addition) appeared to involve only the $\text{Ir}(\text{Me})(\text{PMe}_3)_3$ and/or InMe_3 formed by reversible loss of InMe_3 from **3** and **4**. This is not surprising, as iridium tends to form very stable methyl and hydridomethyl compounds from which methane is evolved only under relatively drastic conditions. However, ethyl compounds of many transition metals are unstable, tending to lose ethylene by β elimination. Therefore, we explored some reactions of Ir compounds with InEt_3 , looking for addition of In–Et bonds and subsequent β elimination.

The reaction between InEt_3 and $\text{IrMe}(\text{PMe}_3)_4$ forms a mixture of compounds. Evidently, there are several separate reactions occurring among several different species, as outlined in eq 7. The most probable initial reaction between $\text{IrMe}(\text{PMe}_3)_4$ and InEt_3 , adding an In–Et bond to iridium, is entirely analogous to the InMe_3 reaction of eq 5. Reversible addition of alkyliridium bonds allows exchange between methyl and ethyl groups, and the resulting ethyl compound $\text{Ir}(\text{C}_2\text{H}_5)(\text{PMe}_3)_4$ decomposes to $\text{IrH}(\text{PMe}_3)_4$ and C_2H_4 .^{10c,d} The liberated ethylene in turn reacts rapidly with $\text{IrMe}(\text{PMe}_3)_4$ to form $\text{IrMe}(\text{C}_2\text{H}_4)(\text{PMe}_3)_3$.^{10b,d} The hydrido compound $\text{IrH}(\text{PMe}_3)_4$ has been shown in separate experiments to react readily with alkylindium compounds, intractably with InMe_3 (see above) but forming primarily one compound with InEt_3 . This compound has been identified as $\text{Ir}(\text{H})(\text{C}_2\text{H}_5)(\text{InEt}_2)(\text{PMe}_3)_3$ (**5**), based on its ^1H and ^{13}C NMR spectra, its reversible reaction with PMe_3 to restore $\text{IrH}(\text{PMe}_3)_4$ and InEt_3 , and its structure as determined by X-ray diffraction (see below). PMe_3 , liberated in the course of the reaction, tends to bind to trialkylindium, displace ethylene from $\text{IrMe}(\text{C}_2\text{H}_4)(\text{PMe}_3)_3$, and provide additional equilibria that further complicate the overall reaction scheme.

As an extension of this work, we looked briefly at reactions between alkylindium and selected platinum compounds. The Pt(0) compound $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ reacts with InMe_3 , releasing ethylene and forming a methylplatinum compound, the NMR spectrum of which is suggestive of $\text{PtMe}(\text{InMe}_2)(\text{PPh}_3)_2$, but the compound decomposes readily. $\text{PtMe}_2(\text{bpy})^{6,13}$ reacts with InMe_3 reversibly

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(13) Kuyper, J. *Inorg. Chem.* **1977**, *16*, 2171–2176. *Ibid.* **1978**, *17*, 77–81. *Ibid.* **1978**, *17*, 1458–1463. Yamashita, H.; Hayashi, T.; Kobayashi, T.; Tanaka, M.; Goto, M. *J. Am. Chem. Soc.* **1988**, *110*, 4417–4418.

(14) Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43–51. Hayes, J. C.; Pearson, G. D. N.; Cooper, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 4648–4650. Hayes, J. C.; Cooper, N. J. *Ibid.* **1982**, *104*, 5570–5572. Jer-nakoff, P.; Cooper, N. J. *Ibid.* **1984**, *106*, 3026–3027. Werner, H.; Kletzin, H.; Hoehn, A.; Paul, W.; Knaup, W.; Ziegler, M. L.; Serhadii, O. *J. Organomet. Chem.* **1986**, *306*, 227–239 and references therein. For an interesting example of alkyl shift from Pb to a transition metal, see: Pannell, K. H. *J. Organomet. Chem.* **1980**, *198*, 37–40.

Table I. Interatomic Distances (Å)

Ir-In	2.601 (1)	P1-C13	1.839 (9)
Ir-P1	2.275 (2)	P2-C21	1.814 (8)
Ir-P2	2.302 (2)	P2-C22	1.812 (8)
Ir-P3	2.309 (2)	P2-C23	1.817 (9)
Ir-C1	2.192 (7)	P3-C31	1.833 (9)
Ir-HIr	1.57	P3-C32	1.827 (9)
In-C3	2.211 (9)	P3-C33	1.800 (8)
In-C5	2.179 (10)	C1-C2	1.438 (12)
P1-C11	1.821 (8)	C3-C4	1.474 (14)
P1-C12	1.820 (8)	C5-C6	1.290 (16)

to form a compound whose ^1H NMR spectrum is consistent with $\text{Pt}(\text{Me})_3(\text{bpy})(\text{InMe}_2)$. NMR spectra of mixtures of InMe_3 and $\text{PtMe}_2(\text{PMe}_3)_2$ or $\text{PtMe}_2(\text{P}(\text{tol})_3)_2$ show only minute shifts, suggesting that an adduct may form reversibly but is not thermodynamically favored.

With InEt_3 , $\text{Pt}(\text{Me})_2(1,5\text{-C}_8\text{H}_{12})$ reacts slowly to form some methylindium compound(s) and $\text{Pt}(\text{Et})_2(1,5\text{-C}_8\text{H}_{12})$. (Likewise, $\text{Pt}(\text{Et})_2(1,5\text{-C}_8\text{H}_{12})$ and InMe_3 form $\text{Pt}(\text{Me})_2(1,5\text{-C}_8\text{H}_{12})$ and ethylindium compounds.) For other platinum compounds $\text{PtMe}_2(\text{bpy})$ and $\text{PtMe}_2(\text{PMe}_3)_2$, there is significant methyl/ethyl exchange between Pt and InEt_3 , although we have not characterized the species present. Also, in each case there is only a small amount of ethylene formed, consistent with the tendency for platinum ethyl groups to undergo rapid β elimination only at elevated temperatures.¹⁵

We also looked very briefly at reactions of rhodium compounds with InMe_3 and of AlMe_3 ¹⁶ and ZnMe_2 with iridium and platinum compounds. ZnMe_2 reacted with $\text{IrMe}(\text{PMe}_3)_4$ to form the *fac* isomer of $\text{Ir}(\text{Me})_2(\text{ZnMe})(\text{PMe}_3)_3$ (**6**), but scouting reactions of ZnMe_2 with $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$, $\text{Pt}(\text{Me})_2(\text{bpy})$, and $\text{Pt}(\text{Me})_2(\text{PMe}_3)_2$ were intractable and were not pursued further. Mixtures of AlMe_3 and $\text{Ir}(\text{Me})(\text{PMe}_3)_4$ in benzene did not form an identifiable adduct, but there were significant shifts in the NMR signals, strongly suggestive of rapid exchange among species such as $\text{Ir}(\text{Me})_2(\text{AlMe}_2)(\text{PMe}_3)_3$, $\text{AlMe}_3\text{PMe}_3$, and/or $\text{Ir}(\text{Me})(\text{PMe}_3)_3\text{AlMe}_3$. $\text{Rh}(\text{Me})(\text{PMe}_3)_4$ and InMe_3 likewise did not form an isolable adduct but did show evidence for reversible adduct formation in solution, with an NMR spectrum nearly identical with that of $\text{Ir}(\text{Me})(\text{PMe}_3)_4\text{-AlMe}_3$ mixtures. $\text{RhH}(\text{PMe}_3)_4$ and InMe_3 reacted immediately, liberating methane, but no other compound could be identified in the resulting complicated mixture.

Structure of Compound 5. Compound **5** is the first crystallographically characterized compound with an In-Ir bond and a rare example of a sterically noncongested 3-coordinate organoindium species.¹⁷ A perspective drawing of the compound is in Figure 1 and bond distances and angles are in Tables I and II.

Coordination about the iridium center is essentially octahedral, as expected for 6-coordinate trivalent iridium. The hydrido hydrogen atom was located, but its position was not refined. Coordination about the indium atom is effectively planar and trigonal, although C1 of the iridium ethyl group is moderately close (3.040 (8) Å). Bond angles about indium are considerably distorted from 120°, in particular C3-In-C5 (104.1 (4)°). This contrasts with $\text{C}_5\text{H}_5(\text{CO})_3\text{WGaMe}_2$, the most closely related compound in the literature, which has angles about the gallium atom very close to 120°.¹⁸ Simplistically, the InEt_2 entity of compound **5** resembles InEt_2^- (isoelectronic with strongly bent stannylene compounds¹⁹) more than it resembles InEt_2^+ (linear like InMe_2^+ ¹²

Table II. Intramolecular Angles (deg)

In-Ir-P1	92.85 (5)	Ir-P1-C13	116.9 (3)
In-Ir-P2	160.41 (6)	Ir-P2-C21	117.4 (3)
In-Ir-P3	93.64 (5)	Ir-P2-C22	119.8 (3)
In-Ir-C1	78.2 (2)	Ir-P2-C23	115.3 (3)
In-Ir-HIr	79	Ir-P3-C31	117.7 (3)
P1-Ir-P2	98.02 (7)	Ir-P3-C32	119.0 (3)
P1-Ir-P3	97.64 (7)	Ir-P3-C33	117.0 (3)
P2-Ir-P3	100.95 (7)	C11-P1-C12	100.5 (4)
P1-Ir-C1	167.6 (2)	C11-P1-C13	98.8 (4)
P2-Ir-C1	88.3 (2)	C12-P1-C13	98.1 (4)
P3-Ir-C1	91.5 (2)	C21-P2-C22	101.0 (4)
P1-Ir-HIr	90	C21-P2-C23	100.3 (4)
P2-Ir-HIr	85	C22-P2-C23	99.9 (5)
P3-Ir-HIr	170	C31-P3-C32	99.2 (4)
C1-Ir-HIr	80	C31-P3-C33	100.5 (4)
Ir-In-C3	124.0 (2)	C32-P3-C33	99.9 (4)
Ir-In-C5	131.8 (3)	Ir-C1-C2	120.0 (6)
C3-In-C5	104.1 (4)	In-C3-C4	118.0 (6)
Ir-P1-C11	115.2 (3)	In-C5-C6	122 (1)
Ir-P1-C12	123.3 (3)		

and isoelectronic R_2Hg compounds). Then bonding in **5** could be described as $^*(\text{H})(\text{Et})\text{Ir}(\text{III})^+ \leftarrow \text{InEt}_2^-$, consistent with the assignment of +3 as the formal oxidation state of iridium.

Compounds having transition metal-indium bonds are well-known,² including compounds with Rh-In or Ir-In bonds,²⁰⁻²² but structures have not been reported for the latter. Without other Ir-In bond lengths for comparison, we cannot say how important π back-bonding might be in determining the Ir-In bond distance (2.601 (1) Å). We note that large thermal motion of the atoms of this low-melting compound may artificially shorten calculated bond lengths, especially C5-C6 (see the Experimental Section).

We also cannot say how important C...In interaction with the iridium ethyl group might be. The orientation of the diethylindium group allows maximum interaction with the iridium ethyl group, and the C1-Ir-In angle (78.2 (2)°) is consistent with some attractive interaction. But note that the *fac*-triphosphine arrangement is rather crowded and P-Ir-P angles approach 100°, so angles among the remaining ligands (H, Et, InEt_2) approach 80° regardless of any incipient bonding interaction. The orientation of the diethylindium group might simply be a steric preference for eclipsing the relatively small Ir-H group. Likewise, the C-C bond of the iridium ethyl group eclipses the metal-hydride bond, as in the related hydridoethyl compound $(\text{PMe}_3)_4\text{Ru}(\text{H})(\text{C}_2\text{H}_5)$.²³

Summary and Conclusions

One aspect of our original interest has been addressed, and we now know that alkyl-indium bond cleavage can be achieved under very mild conditions using transition-metal compounds. With organoiridium compounds the predominant reaction is direct "oxidative addition" of the alkyl-indium bond. The reactions are reversible, and trialkylindium can be displaced from the iridium compound by adding ligands (PMe_3 , C_2H_4) that bind to iridium (and, to some extent, trialkylindium). In the case of organoplatinum compounds, such addition reactions tend to be less favored, and adducts are observed only in certain cases. However, the addition products readily undergo exchange reactions with alkyl groups already present in the iridium or platinum substrate, allowing further sequences of reactions that can become complicated (e.g. eq 7). Other main-group alkyl compounds react similarly with organoiridium and -platinum compounds, as already reported in the literature and as we have observed for dimethylzinc.

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Table III. ^1H NMR Data^a for Methyl Compounds

compd (solvent)	PMe_3	IrMe	$(\text{In,Zn})\text{Me}$
<i>mer</i> - $\text{Ir}(\text{Me})_2(\text{InMeBr})(\text{PMe}_3)_3$ 1 (py- <i>d</i> ₃)	1.42 (18 H, t, 3.2) 1.48 (9 H, d, 7.7)	-0.11 (3 H, q, 6.7) +0.06 (3 H, t, 8.1, of d, 4.6)	0.30 (3 H, s)
<i>fac</i> - $\text{Ir}(\text{Me})_2(\text{InMeBr})(\text{PMe}_3)_3$ 2 (py- <i>d</i> ₃)	1.10 (9 H, d, 7.5) 1.53 (18 H, d, 7.5)	+0.14 (6 H, d, 11.5, of q, 3.2)	0.42 (3 H, d, 1.5)
<i>fac</i> - $\text{Ir}(\text{Me})_2(\text{InMe}_2)(\text{PMe}_3)_3$ 3 (C_6D_6)	0.90 (9 H, d, 7.0) 1.14 (18 H, d, 6.8)	+0.12 (6 H, d, 11.9, of q, 3.5)	0.38 (6 H, s) ^b
<i>mer</i> - $\text{Ir}(\text{Me})_2(\text{InMe}_2)(\text{PMe}_3)_3$ 4 (C_6D_6)	1.10 (18 H, t, 2.9) 1.13 (9 H, d, 7.4)	-0.11 (3 H, d, 6.9, of t, 6.0) +0.25 (3 H, t, 8.2, of d, 4.6)	0.38 (s) ^b
<i>fac</i> - $\text{Ir}(\text{Me})_2(\text{ZnMe})(\text{PMe}_3)_3$ 6 (C_6D_6)	0.93 (9 H, d, 6.2) 1.22 (18 H, d, 6.2)	+0.40 (6 H, d, 13.1, of q, 3.5)	0.04 (3 H, s)

^aChemical shifts in ppm downfield from external Me_4Si . Coupling constants in hertz. ^bSignal can appear at 0.03 if traces of excess InMe_3 -ether are present.

Experimental Section

Owing to the extremely air- and moisture-sensitive nature of main-group metal alkyl and alkyliridium(I) compounds, all compounds were prepared, stored, and handled under an inert atmosphere, generally in a glovebox under nitrogen. Note particularly that alkylindium, alkylaluminum, and alkylzinc compounds are *pyrophoric* in air and evolve flammable gases when exposed to moisture. Solvents were dried using standard methods. Triethylindium, trimethylaluminum, and dialkylzinc compounds were obtained commercially. Methyltetrakis(trimethylphosphine)iridium and -rhodium were prepared as in previous work;^{16,24} trimethylindium, bromodimethylindium, trimethylindium etherate,²⁵ and platinum compounds²⁶⁻²⁸ were prepared by modifications of literature methods. Ambient-temperature NMR spectra were obtained with GE QE-300 instruments. ^1H NMR data for iridium methyl compounds are presented in Table III.

(Bromomethylindium)dimethyltris(trimethylphosphine)iridium(III), *mer* isomer 1: A mixture of 0.04 g of BrInMe_2 and 0.095 g of $\text{IrMe}(\text{PMe}_3)_4$ in benzene was stirred for 30 min and filtered, collecting 0.01 g of white solid (an impure mixture of compounds 1 and 2 by ^1H NMR). The filtered solution slowly deposited additional solid, which was collected after 90 min; estimated yield 0.02 g of pure *mer* compound 1 (^1H NMR, py-*d*₃; see Table III).

fac isomer 2: The reagents were combined in ether, and 0.07 g of white powder was collected after 30 min (57% of pure *fac* isomer by ^1H NMR, py-*d*₃). In pyridine solution each compound slowly isomerized, after 2 days reaching an equilibrium mixture of compounds 1 (25%) and 2 (75%).

(Dimethylindium)dimethyltris(trimethylphosphine)iridium(III), *fac* and *mer* isomers (3,4): $\text{IrMe}(\text{PMe}_3)_4$ (0.027 g) and InMe_3 -ether (0.010 g) were combined in 1 mL of C_6D_6 . Compounds 3 and 4, PMe_3 , and ether were the only species present (^1H NMR). The solution was evaporated, and the residue was redissolved in warm pentane and cooled to -30°C . After 1 day 0.02 g of flaky white solid was collected. When redissolved in C_6D_6 , the material was entirely compounds 3 (88%) and 4 (12%) by ^1H NMR (Table III). After bubbling ethylene through the solution briefly, the ^1H NMR spectrum revealed the presence of significant amounts (ca. 40%) of the ethylene adduct $\text{IrMe}(\text{C}_2\text{H}_4)(\text{PMe}_3)_3$ ^{10b,d} and "free" InMe_3 . Allowing ethylene to dissipate into a nitrogen atmosphere restored compounds 3 and 4.

(Diethylindium)ethylhydridotris(trimethylphosphine)iridium(III) (5). $\text{IrH}(\text{PMe}_3)_4$ ²⁹ (0.10 g) and InEt_3 (0.04 g) were dissolved in benzene. After standing 10 min at room temperature, the solution was evaporated, and the oily residue was dried (10^{-3} Torr, 30 min) and redissolved in ca. 0.5 mL of pentane. Refrigeration at -30°C for 2 days produced 0.025 g of pale yellow, transparent crystals that melted when warmed to room temperature. Crystallized material was used for the reported NMR data, but NMR spectra of crude reaction mixtures were quite similar. ^1H NMR of 5 (C_6D_6 , chemical shifts in ppm downfield from external Me_4Si , multiplicities and coupling constants (Hz) in parentheses) Hir , -11.6 [d (123) of t (17)]; $(\text{H}_3\text{C})_3\text{P}$, 1.16 (d, 7.5), 1.17 (d, 7.3), 1.25 (d, 7.4); ethyl H, 1.1 (br m), 1.3 (br m), 1.86 (br, pseudo q, 8). $\{^1\text{H}\}^{13}\text{C}$ NMR of 5: IrCH_2 , -22.11 [d (64.4) of t (6.3)]; IrCH_2CH_3 , 30.19 (d, 13.2); InCH_2 , 18.92 (d, 21.9); InCH_2CH_3 , 12.80 (s); $\text{P}(\text{CH}_3)_3$, 21.75 (d, 23.2), 22.75 (d, 25.9), 28.46 (d, 20.8). Treating solutions of compound 5 with PMe_3

Table IV. Crystal and Refinement Data for Compound 5

compd	$\text{IrH}(\text{C}_2\text{H}_5)(\text{In}(\text{C}_2\text{H}_5)_2)(\text{PMe}_3)_3$
formula	$\text{C}_{15}\text{H}_{43}\text{In}_1\text{Ir}_1\text{P}_3$
formula wt	623.45
<i>a</i> , Å	14.836 (3)
<i>b</i> , Å	14.658 (3)
<i>c</i> , Å	11.022 (2)
β , deg	90.22 (1)
<i>V</i> , Å ³	2396.9
<i>Z</i>	4
space gp	$P2_1/n$ (No. 14)
ρ (calc), g/cm ³	1.727
cryst dimens, mm	0.36 × 0.30 × 0.50
temp, °C	-100
radiatn	Mo $K\alpha$ from graphite monochromator
μ , cm ⁻¹	66.66
total no. of reflectn	3614 unique with $I > 3\sigma$
final no. of variables	181
<i>R</i>	0.034
<i>R</i> _w	0.033
error of fit	1.19

Table V. Fractional Coordinates (×10000) and Isotropic Thermal Parameters

atom	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>B</i> _{iso}
Ir	1410.7 (2)	2226.6 (2)	2523.4 (2)	2.4 (1)'
In	1581.3 (5)	2480.2 (4)	200.4 (5)	4.2 (1)'
P1	252 (1)	1226 (1)	2274 (2)	3.3 (1)'
P2	1768 (1)	1871 (1)	4502 (2)	3.3 (1)'
P3	557 (1)	3528 (1)	2792 (2)	3.5 (1)'
C1	2657 (5)	3027 (5)	2438 (8)	4.4 (2)'
C2	3498 (7)	2584 (7)	2171 (14)	8.9 (5)'
C3	2129 (7)	1449 (7)	-1062 (8)	6.5 (3)'
C4	2461 (7)	583 (7)	-548 (9)	6.2 (3)'
C5	1338 (12)	3669 (7)	-941 (10)	10.4 (5)'
C6	932 (13)	3605 (9)	-1975 (11)	13.7 (7)'
C11	543 (5)	31 (5)	2497 (8)	4.4 (2)'
C12	-793 (5)	1291 (6)	3130 (9)	5.8 (3)'
C13	-244 (6)	1143 (6)	746 (9)	5.1 (3)'
C21	2352 (6)	2732 (6)	5387 (7)	5.6 (3)'
C22	884 (6)	1541 (6)	5545 (7)	5.3 (3)'
C23	2533 (7)	914 (6)	4695 (8)	5.9 (3)'
C31	-413 (6)	3699 (6)	1781 (9)	6.1 (3)'
C32	4 (6)	3715 (6)	4249 (9)	5.7 (3)'
C33	1125 (6)	4605 (5)	2621 (9)	5.6 (3)'
Hir	2102	1454	2196	4.0

restored $\text{IrH}(\text{PMe}_3)_4$ and $\text{InEt}_3 \cdot x\text{PMe}_3$.

(Methylzinc)dimethyltris(trimethylphosphine)iridium(III) (6). $\text{IrMe}(\text{PMe}_3)_4$ (0.050 g) and Me_2Zn (0.012 g) were combined in C_6D_6 . The NMR spectrum showed essentially quantitative formation of 6, but the MeZn signal was very broad. The solution was evaporated and the residue redissolved in C_6D_6 ; the ^1H NMR signals were then much sharper. Very small amounts, ca. 5%, of a second compound could be discerned, NMR signals of which are consistent with a *mer* isomer of 6.

Reaction of Trimethylindium with Dimethylbipyridylplatinum(II). PtMe_2bpy (0.008 g) in C_6D_6 was treated with excess InMe_3 -ether, immediately depositing a yellow solid. After recrystallization from hot benzene, its ^1H NMR spectrum (dilute C_6D_6) showed unreacted PtMe_2bpy (PtMe , chemical shift 1.70) (ca. 33%), $\text{PtMe}_3(\text{InMe}_2)$ - $(\text{bpy})(\text{PtMe}$, 0.18, 1.67) (ca. 67%), and InMe_x (-0.20).

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X-ray Structure of Compound 5. Working in a drybox, under a stream of cold (ca. $-20\text{ }^{\circ}\text{C}$) nitrogen gas to prevent melting, a single crystal of compound **5** was loaded into a capillary and sealed with wax. It was quickly transferred to the diffractometer and cooled to $-100\text{ }^{\circ}\text{C}$ in a N_2 stream. Space group, unit cell, and data collection information are provided in Table IV. The solution and refinement were uneventful, except for the hydrido hydrogen atom, which tended to refine to an unacceptably short Ir–H separation. This atom was held fixed at its Fourier difference map position. Remaining hydrogen atoms were placed in idealized locations. Consistent with the low melting point of the material, there is considerable apparent thermal motion of several of the atoms, most notably C5 and C6 of the indium ethyl group. As a result of this thermal anisotropy, the calculated C5–C6 bond distance is unrealistically short (1.29 (2) Å). Being suspicious that this might indicate a vinyl group, formed by metal-catalyzed dehydrogenation, we analyzed the remaining crystals from this batch ($^1\text{H NMR}$, C_6D_6) but found absolutely no evidence for a vinyl group nor for any compound other than **5**. Final refinement data is included in Table IV. Largest residual

density in the final difference Fourier map is $1.42\text{ e}/\text{\AA}^3$ near the indium atom. Bond distances and angles are listed in Tables I and II. Non-hydrogen atom positions are listed in Table V. Anisotropic thermal parameters, hydrogen atom positions, a listing of F_{obs} vs F_{calc} (Tables 6–8), and a stereodrawing of the unit cell (Figure 2) are available as supplementary material.

Acknowledgment. The crystal of compound **5** was skillfully mounted by L. Lardear. We also thank L. Ayers for technical assistance and P. Fagan and R. T. Baker for communicating results prior to publication.

Supplementary Material Available: Tables of anisotropic thermal parameters (Table 6) and hydrogen atom parameters (Table 7) and a stereodrawing of the unit cell (Figure 2) (3 pages); listing of F_{obs} vs F_{calc} (Table 8) (3 pages). Ordering information is given on any current masthead page.

A Short, Enantioselective Synthesis of (–)-Swainsonine¹

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Abstract: A practical, enantioselective synthesis of (–)-swainsonine (**1**) has been achieved in seven steps from 2,3-*O*-isopropylidene-D-erythrose (**6**). The key step involves the construction of the bicyclic imine **4** by an intramolecular 1,3 dipolar cycloaddition of azide **5**. This study highlights the synthetic utility of the intramolecular 1,3 dipolar cycloaddition of the unactivated olefinic azides in natural product synthesis.

From the fungus *Rhizoctonia leguminicola* there was isolated a toxic indolizidine alkaloid, swainsonine (**1**).³ Swainsonine has also been shown to be present in locoweed (*Astragalus lentiginosus*^{4a}) and *Swainsona canescens*,^{4b} as well as in the fungus *Metarhizium anisopliae*.⁵ The pronounced α -mannosidase inhibitory⁶ and immunoregulative^{5,7} properties of swainsonine have stimulated considerable interest in biosynthetic⁸ and pharmaco-

(1) A preliminary account of this work was presented in part at the 16th International Symposium on the Chemistry of Natural Products, Kyoto, Japan, May 29–June 3, 1988 and at the 3rd Chemical Congress of North America, Toronto, Canada, June 1988.

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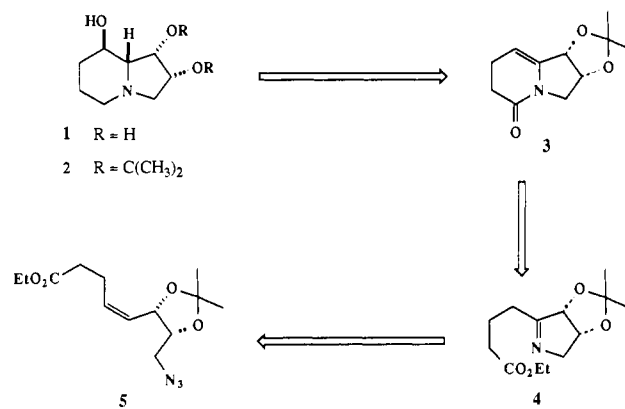
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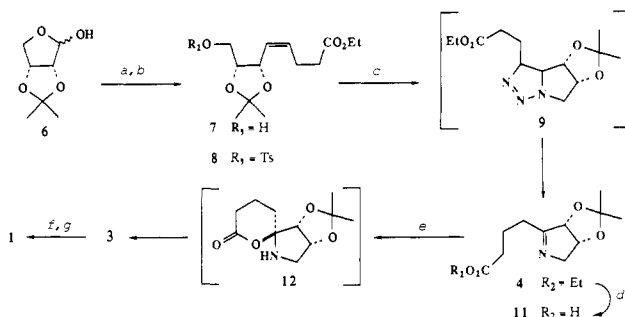
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Scheme I



Scheme II^a



^a Reagents and conditions: (a) $\text{Br}^+\text{Ph}_3\text{P}^+\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{Et}$, $\text{KN}(\text{TMS})_2$, THF, $-78\text{ }^{\circ}\text{C}$; (b) *p*-TsCl, Et_3N , CH_2Cl_2 ; (c) NaN_3 , DMF, $70 \rightarrow 100\text{ }^{\circ}\text{C}$; (d) K_2CO_3 , aqueous MeOH, room temperature; (e) toluene, reflux; (f) BH_3 , THF/ H_2O_2 -NaOH; (g) 6 N HCl, THF.

logical⁹ studies, and its total synthesis has been achieved by several groups.¹⁰ As demand for swainsonine in cancer research remains