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Correspondence

Improved Isolation Procedure for the Preparation of Iodo(trimethyl)platinum(IV)

AIC50149D

Sir:

The standard method for the preparation of iodo(trimethyl)platinum(IV) has been that of Clegg and Hall[1] which typically uses 10 g of potassium hexachloroplatinate and twice the stoichiometric quantity of methyl Grignard reagent. Our repeated attempts to reproduce this synthesis on a smaller scale with less than 10 g of potassium hexachloroplatinate have led to little or no product.

Decomposition of the excess Grignard reagent with cold 10% HCl solution invariably has given orange and black insoluble products which are the dimethylplatinum diiodide complex and platinum iodides,[2] respectively. Repeated extraction of the orange-black mixture with benzene at reflux gives less than 2% of iodo(trimethyl)platinum(IV) iodide. The present method ensures the removal of the magnesium salts by filtration of the reaction mixture prior to decomposition of excess Grignard reagent. Then the clear filtrate is decomposed with acetone instead of 10% HCl. The *tert*-butyl alcoholate which is formed from interaction with acetone and excess Grignard reagent serves to complex magnesium iodides. These are then dissolved in a normal fashion with dilute HCl and the product is isolated from the benzene layer.

Since other workers[3] have apparently experienced similar difficulties, the following procedure is submitted. Adherence to this work-up gives consistently 80–82% of a pure product.

Experimental Work. Potassium chloroplatinate, K_2PtCl_6,[4] is dried overnight at 110° under reduced pressure (about 0.2 Torr). Diethyl ether and benzene, both Mallinckrodt AR grade, are dried by distillation under argon immediately prior to use from lithium aluminum hydride and sodium diethylaluminum dihydride, respectively. Methyl iodide, Mallinckrodt AR grade, was distilled from anhydrous $CaSO_4$ under nitrogen and stored under nitrogen until used.

The Grignard reagent, CH_3MgI, is prepared by dropping 5.0 ml (11.4 g, 80 mmol) of methyl iodide in 20 ml dry ether onto 1.10 g (45.2 mmol) of flame-dried magnesium turnings under nitrogen. The alkyl halide solution is added at a rate to maintain a steady reflux; the addition requires about 20 min. The resulting black suspension is then stirred until the last pieces of magnesium are dissolved and filtered through a sintered-glass disk (medium porosity) directly into a dropping funnel mounted atop a flask which contains 2.00 g (4.12 mmol) of finely powdered K_2PtCl_6.[5]

The Grignard reagent is then added dropwise over a 10-min period to an ice-cooled suspension of K_2PtCl_6 in 10 ml of ether and 40 ml of benzene. The reaction mixture is allowed to warm gradually to room temperature after the addition and is left to stir under nitrogen. Within 4 hr the mixture fades from yellow to white.

After stirring the mixture overnight, the white salts are allowed to settle. The supernatant is then filtered through a medium sintered-glass disk under nitrogen. The clear, nearly colorless filtrate (not orange as previously described[1]) is cooled to 0° and 5 ml of ice-cold acetone is slowly added dropwise to the stirring filtrate. As the acetone is added a vigorous reaction takes place, which turns the mixture yellow and then orange. A two-phase mixture results with a yellow layer at the top and an orange layer below.

After opening the flask to the air, 25 ml of ice-cold water is added to the stirring mixture, which coagulates the bottom layer into a light yellow solid and produces an orange supernatant. This mixture is acidified with 30 ml of 10% HCl which dissolves the solid and gives an orange-yellow organic layer over a pinkish orange aqueous layer with a small amount of orange solid at the interphase. The orange solid is filtered and the layers are separated. The aqueous layer is extracted with 3 30-ml aliquots of benzene. After extraction the aqueous layer is the color of claret. The extracts are combined with the organic layer and dried by filtration through a cone of anhydrous $CaSO_4$. The clear, yellow-orange solution is then rotary evaporated to dryness and the resulting yellow solid is dissolved in 30 ml of $CHCl_3$. This solution is evaporated to about 15 ml on the hot plate, 15 ml of acetone is added, and the mixture is cooled in ice. The yellow crystals formed are collected with suction and air-dried. The yield is 1.21–1.22 g (80–81%), mp 195° dec; ir and NMR data are identical with those reported in the literature.[6]

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Registry No. Iodo(trimethyl)platinum(IV), 14364-93-3; K_2PtCl_6, 16921-30-5; CH_3MgI, 917-64-6.

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Tin–Halogen Stretching Frequencies and the Hard and Soft Acid–Base Theory

AIC50117Q

Sir:

Since the proposal of the HSAB theory,[1] at least two papers have shown that, in the application toward certain areas, the HSAB fails.[2,3] In a recent report by Ohkaku and Nakamoto[4] it was pointed out that the Sn–X stretching frequency is sensitive to the nature of the donor ligands in compounds of formula SnX_4L_2 or SnX_4L-L. The observation was made that the Sn–X bond becomes stronger as the Sn–L bond becomes weaker. On that basis, the order of metal–ligand force constant

Table I. Range of Sn-X Stretching Frequencies for Some $SnX_4 \cdot 2L$ Complexes

SnX_4	Ligand[a]	Classification	Range of ν(Sn-X) absorption, cm^{-1}	Ref
cis-$SnCl_4$	DME	Hard	340-325	5
	2 AA	Hard	341-305	6
	2 DMF	Hard	340-313	7
	TMEN	Hard	325-300	8
	bipy	Borderline	333-284	9
	phen	Borderline	341-278	9
	PN	Borderline[b]	325-309	10
	DP	Soft	323-305	10
	diphos	Soft	320-297	9
	DTH	Soft	326-288	9
trans-$SnCl_4$	2 THF	Hard	342	4
	2 DAA	Hard	328	6
	2 py	Borderline	323	4
	2 THT	Soft	318	4
	2 TPA	Soft	309	4
	2 TPP	Soft	307	4
cis-$SnBr_4$	DME	Hard	250-220	5
	2 DMF	Hard	249-216	7
	TMEN	Hard	230-209	8
	bipy	Borderline	258-218	9
	phen	Borderline	244-226	9
	PN	Borderline[b]	216-203	10
	DP	Soft	234-208	10
	diphos	Soft	233-207	9
	DTH	Soft	246-216	9
trans-$SnBr_4$	2 THF	Hard	247	4
	2 py	Borderline	247, 231	4
	2 THT	Soft	218	4
	2 TPP	Soft	209	4
cis-SnI_4	TMEN	Hard	170-136	8, 11
	2 HQ	Hard[c]	178-140	12
	bipy	Borderline	196-173	9
	phen	Borderline	195-191	9
	PN	Borderline[b]	194-139	10
	DP	Soft	205-167	10
	diphos	Soft	190-180	8
	DTH	Soft	182-170	9
trans-SnI_4	2 $N(CH_3)_3$	Hard	158-142	11
	2 py	Borderline	195-185	4

[a] Abbreviations: DME, 1,2-dimethoxyethane; AA, acrylamide; DMF, *N,N*-dimethylformamide; TMEN, *N,N,N',N'*-tetramethylethylenediamine; bipy, 2,2'-bipyridyl; phen, 1,10-phenanthroline; PN, *o*-$C_6H_4(PPh_2)N(CH_3)_2$; DP, *o*-$C_6H_4(PPh_2)_2$; diphos, 1,2-bis(diphenylphosphino)ethane; DTH, 2,5-dithiahexane; THF, tetrahydrofuran; DAA, *N,N*-dimethylacrylamide; py, pyridine; THT, tetrahydrothiophene; TPA, triphenylarsine; TPP, triphenylphosphine; HQ, 8-hydroxyquinoline. [b] The molecule contains a hard and soft donor and is arbitrarily classified as borderline. [c] Coordination through oxygen assumed; stereochemistry not assigned.

on $SnCl_4$ decreased in the order $PPh_3 > AsPh_3 >$ THT > py > THF (where THT = tetrahydrothiophene).

This order appears to be the opposite of what would be predicted according to HSAB principles. Tin(IV) in $SnCl_4$ is hard and would be expected to form the strongest bond with THF; i.e., the reverse order of force constants from that shown above would be expected.

However, if one examines the Sn-X stretching frequencies with respect to the nature of the other donor ligands, then a result consistent with HSAB theory is observed. Table I shows the pertinent data.

Upon examination of the range of absorption of ν(Sn-X) one observes that, for $SnCl_4$ complexes, the Sn-Cl frequencies are highest where the coordinated ligands are hard, intermediate with borderline ligands, and lowest where soft donors are coordinated. This is true for both cis and trans complexes. The $SnBr_4$ complexes are not quite as clear-cut, where the Sn(IV) acid center in these complexes would be expected to be somewhat softer than in the tetrachloride. For $SnBr_4$ complexes, it is the general trend that the strongest Sn-Br bond strength occurs in the presence of hard and borderline bases. The SnI_4 complexes, where the acid center is still softer than the others, shows the highest Sn-I absorption where the coordinated ligands are borderline or soft.

It is clear, therefore that for *cis*- and *trans*-$SnCl_4L_2$ and -$SnCl_4LL$ complexes, the Sn-Cl stretching frequencies decrease in the order of coordinated ligand: hard > borderline > soft. For the corresponding bromide complexes, the order appears to be hard ~ borderline > soft. Whereas there exists a paucity of infrared spectral information on complexes of SnI_4 with hard bases, for those few examples reported, the trend for the corresponding iodide complexes is opposite that of the chloride complexes, i.e., hard < borderline ~ soft.

Whereas the observation made by Ohkaku and Nakamoto that the SnX bond becomes stronger as the SnL bond becomes weaker may hold, the more useful statement (for prediction and band assignment purposes) may be made that the tin-halide stretching frequencies will be higher where the coordinated ligand is more like the halide in terms of hardness or softness.

Registry No. Tin, 7440-31-5.

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Atomization Enthalpy of Europium Trichloride

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Sir:

In a recent note on bonding models for lanthanide trihalides,[1] the calculated enthalpy for the reaction

$$\mathrm{EuCl_3(g) = Eu^*(g) + 3Cl(g)} \quad \Delta H_{\mathrm{at}}^* = 387 \text{ kcal/mol} \qquad (1)$$

was noted to be anomalously high. It has been pointed out[2] that the difficulty lies with the value of the enthalpy of formation of $EuCl_3$(s) used in calculating ΔH_{at}^* and *not* with the enthalpy of sublimation of europium[3] nor with the promotion energy ($d^2s \leftarrow$ ground state) of the europium atom.[4] When the more recent and reliable value,[5] $\Delta H_f^\circ(\mathrm{EuCl_3(s)}) = -223.7$ kcal/mol, is used, a revised value of the enthalpy of reaction 1, $\Delta H_{\mathrm{at}}^* = 364$ kcal/mol, is obtained which removes the apparent anomaly. The irregularities in ΔH_{at}^* for EuX_3 (X = F, Br, I) molecules are due to an error in the estimated enthalpies of formation[6] which assumed $\Delta H_f^\circ(\mathrm{LnX_3(s)})$ to vary smoothly across the lanthanide series.

In summary, the apparent anomaly in the values of $\Delta H_{\mathrm{at}}^*(\mathrm{EuX_3})$ has been removed and there is no need to question either the enthalpy of sublimation of europium or the valence-state promotion energy of the europium atom.