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Immobilization, Stabilization, and Isolation of Organocopper Compounds Using Solid Supports

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The value of organocopper compounds as synthetic intermediates is well established.[1] These compounds are sensitive to temperature, oxygen, and moisture and are usually generated in situ at low temperatures (−70 to 0 °C) and must be used immediately. Better product yields could be obtained if these reactions could be carried out at higher temperatures. Certain reactions of organocopper compounds such as those with epoxides are required to be carried out at 0 °C and higher to obtain any significant product yields. It is thus desirable to develop methods that would enable the stabilization, isolation, and long-term storage of organocopper compounds without loss of their stereospecific reactivities. Ligands like phosphines and sulfides have been shown to improve the stabilities of in situ prepared organocopper compounds.[2] Recently Lipshutz has developed a stable lower order cuprate, lithium (2-thienyl)cyanocuprate, with which higher order cuprates can be conveniently generated.[3] The addition of stabilizing ligands introduces the problem of their separation from the products. The use of polymeric supports like polystyrene derivatized with these stabilizing ligands to immobilize organocopper compounds would avoid this problem, provided the stereospecific reactivities of the organocopper compounds are preserved. Polymeric supports are capable of stabilizing sensitive organometallic species such as those of Rh(I) and Pd(0) by reducing their sensitivities to temperature, moisture, and oxygen.[4] Immobilization of organocopper compounds on polymeric supports should also minimize their aggregation due to reduced intermolecular interactions, leading to their enhanced reactivities. The case of $LiCu(CH_3)_2$, which is dimeric in solution and forms poorly reactive $Li_2Cu_3(CH_3)_5$ during the course of its reactions with organic substrates, illustrates this problem.[5]

A limited number of studies were undertaken by San Filippo to immobilize $LiCuR_2$ (R = CH_3, *n*-butyl, *sec*-butyl, and *tert*-butyl) on polystyrene containing PPh_3 stabilizing ligand.[6] It was found that the polymer-supported reagents reacted with alkyl halides and α,β-unsaturated carbonyl compounds. Substantial leaching of the bound $LiCuR_2$ was found to occur, and the polymer-bound species were not separated from the species in solution. As a result the reactivities and stabilities of the polymer-bound species in the absence of the solution species were not determined. In our preliminary studies, we have successfully immobilized, stabilized, and isolated organocopper species $LiCuR_2$ (R = CH_3 and *n*-butyl (*n*-Bu)) using polystyrene and polyethylene derivatized with PPh_2 and 2,2′-bipyridyl (bpy) ligands. We have shown that these isolated polymer-bound organocopper species react quantitatively with alkyl halides and are stable for periods of weeks at room temperature under Ar. The results of our studies are described.

Experimental Approach

CuI (Aldrich, 98%) was used in our studies and was purified by a slight modification of the procedure of Kauffman.[7] All operations were carried out under Ar. A 2.3-g amount of the commercial CuI was dissolved in a solution of 23 g of KI in 20 mL of H_2O, and this solution was slowly diluted with H_2O until the CuI was obtained as a white precipitate. It was collected by filtration and the above procedure repeated one more time. The collected CuI was washed with absolute alcohol and dried under vacuum. It was stored in the refrigerator for use in the preparation of organocopper compounds. Polystyrene cross-linked with 2% divinylbenzene (DVB) (200–400 mesh), soluble polystyrene, and polyethylene from Polyscience Corp. were used in our studies. All solvents were analytical grade and were appropriately distilled and dried. Polystyrene with 2% DVB was cleaned according to the published procedure.[8] Soluble polystyrene was dissolved in CCl_4 and poured into methanol to obtain a white powder. This procedure was repeated three times, and the polymer was dried under vacuum at 60 °C for 12 h. PPh_2 and bpy were bound to polystyrene and polyethylene by using literature methods.[8-10] Each polymer was brominated, and the brominated polymer was used to bind the PPh_2 and bpy ligands. The amount of these ligands bound to the polymeric supports was estimated by elemental analysis of P, N, and C (Atlantic Microlabs, Atlanta, GA, and Midwest Microlab, Indianapolis, IN). The bpy groups were also estimated by the amount of Fe^{3+} bound from tetrahydrofuran (thf).[10] This value was 85% of the value obtained from elemental analysis and was taken to represent the available bpy groups for organocopper binding in thf and diethyl ether. The organocopper species $LiCuR_2$ (R = CH_3, *n*-Bu) were attached to the polymers bearing L (L = PPh_2, bpy) by the procedures in eq 1 and 2. A 4-fold excess of $LiCuR_2$ compared to L was employed in the procedure in eq 1. However, only 2 mol of LiR/mol of LCuI was employed in the procedure in eq 2 in order to obtain $LiCuR_2$ as the polymer-bound species. $LiCuR_2$ for eq 1 was prepared by the addition of 2 mol of LiR to 1 mol of purified CuI. $\textcircled{P}$–CuI was prepared by treating $\textcircled{P}$–L with $[(n\text{-}Bu)_2S]CuI$, which was synthesized according to the procedure of Kauffman.[7] The amount of CuI bound to the polymer was determined by the analysis of I and Cu. Analysis of Cu was carried out by treating the polymer with concentrated HNO_3 to strip Cu(I), concentrating the HNO_3 solution, making up the solution to a known volume, and estimating the Cu by ICP-AES (inductively coupled plasma atomic emission spectroscopy) using the 224.7-nm emission line. Iodine was determined by routine elemental analysis. The amount of Cu and I indicated that the bound species was CuI. The equilibration of the polymer with the respective solution species (eq 1 and 2) were carried out at 0 °C for 4 h. The mixture was centrifuged at room temperature and washed thrice with freshly distilled and degassed thf. Examination of the washings by ^1H NMR revealed a peak at −1.2 ppm in the case of $LiCu(CH_3)_2$, indicating leaching of these species from the polymer backbone. The thf solution when treated with 1-iodooctane yielded nonane in the case of $LiCu(CH_3)_2$ and dodecane in the case of $LiCu(n\text{-}Bu)_2$. A blank experiment was performed in which the polymer without the stabilizing ligand L was equilibrated as in eq 1 and 2 and separated from the reagent. The separated polymer was washed with thf thrice and the washings reacted with 1-iodooctane. The amounts of nonane and dodecane formed were taken to represent the blank value and subtracted from the values of the alkanes obtained after washing the polymer bearing $LiCuR_2$. The differences indicated the extent of leaching of the respective organocopper compounds. The polymer obtained after washing was kept under vacuum at room temperature for 12 h. The dry polymer bearing $LiCuR_2$ was stored under Ar at 0 °C. Samples were taken and kept at room temperature under Ar for evaluation of their thermal stabilities.

$$\textcircled{P}\text{–L} + LiCuR_2 \rightleftharpoons [\textcircled{P}\text{–L–}CuR_2]Li \qquad (1)$$

$$\textcircled{P}\text{–LCuI} + 2\,LiR \rightleftharpoons [\textcircled{P}\text{–L–}CuR_2]Li \qquad (2)$$

The amount of $LiCuR_2$ intact on the polymer was determined by reacting the polymer with an excess of 1-iodooctane in thf at room temperature for 2 h as in eq 3. The solution was analyzed by gas chromatography using conductivity detection and a 10% SE-30 on Chromosorb W-HP (Alltech) column at a temperature of 125 °C and He carrier gas flow of 60 mL/min. The amounts of nonane and dodecane obtained when the bound $LiCu(CH_3)_2$ and $LiCu(n\text{-}Bu)_2$ were reacted with 1-iodooctane were determined by injecting thf solutions containing known amounts of these alkanes. The amounts of nonane and dodecane were taken to represent the amounts of $LiCu(CH_3)_2$ and $LiCu(n\text{-}Bu)_2$ bound

$$[\textcircled{P}\text{–LCuR}_2]Li + CH_3(CH_2)_7I \rightarrow \textcircled{P}\text{–LCuR} + LiI + CH_3(CH_2)_7R \qquad (3)$$

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Table I. Extent of Derivatization of Polymeric Supports

polymer	group	amt of group, mmol/g of support
polystyrene (2% DVB)	Br	4.0
	PPh_2	2.5
	PPh_2CuI	1.4
	bpy	2.0
	bpyCuI	1.6
polyethylene	Br	4.5 (1 Br/4 C)
	PPh_2	2.8
	PPh_2CuI	1.8
	bpy	3.0
	bpyCuI	2.5
polystyrene (soluble)	Br	3.0
	PPh_2	2.0
	PPh_2CuI	1.5

to the polymer. The polymer remaining after the reaction with 1-iodooctane was subject to complete elemental analysis as before, which indicated the polymer-bound species to be CuR, confirming the stoichiometry in eq 3. Some of this material was treated with LiR to explore the possibility of regenerating $LiCuR_2$ on the polymer. The regeneration was approximately 40% of the original amount of $LiCuR_2$ in the case of PPh_2 ligand and 60% in the case of bpy ligand but 90% based on the Cu content obtained from elemental analysis after reaction with 1-iodooctane. The reason for the incomplete regeneration of these species is due to the leaching of $LiCuR_2$ during their reactions with 1-iodooctane, as discussed below. This experiment demonstrates that these polymeric materials can be repeatedly used for the regeneration of $LiCuR_2$ and that 1-iodooctane is consumed by $LiCuR_2$ both bound to the polymer and leaching into solution.

Results and Discussion

Table I contains the extent of derivatization of each polymer with the respective functional groups. These values are comparable to those reported in the literature.[8-11] It is evident from this table that the amount of CuI attached to PPh_2 and bpy on the three polymers is less than the number of available PPh_2 and bpy ligands. This indicates either that there is incomplete functionalization or that some of the CuI is bound to more than one site. Multisite attachment is more probable in the case of PPh_2 than in the case of bpy.

The loading capacities for freshly bound $LiCu(CH_3)_2$ and $LiCu(n\text{-}Bu)_2$ as determined by the amounts of nonane and dodecane respectively are listed in Table II. It may be seen that the direct interaction of the derivatized polymeric support as in eq 1 with the respective $LiCuR_2$ consistently yielded higher loading capacities for these species than the method in eq 2, reported by San Filippo, where the bound CuI was reacted with the respective LiR. Both methods, however, loaded less $LiCuR_2$ than the available PPh_2 or bpy groups. A major cause for this was the leaching of these species from the polymer backbone during washing of the polymer with thf to remove excess $LiCuR_2$ or LiR, as the case may be. Treatment of the thf washings with 1-iodooctane yielded nonane and dodecane for $LiCu(CH_3)_2$ and $Li(n\text{-}Bu)_2$, respectively. As mentioned in Experimental Approach, examination of the thf solution by ^1H NMR in the case of $LiCu(CH_3)_2$ also showed a peak at −1.2 ppm indicating the presence of $[LiCu(CH_3)_2]_2$. Even though the solution species is dimeric, the polymer-bound species is monomeric as indicated by elemental analysis and the yields of nonane and dodecane. The extent of leaching of $LiCuR_2$ species could be quantitated from the amounts of nonane and dodecane formed from the washings as described in Experimental Approach. Comparison of the amounts of nonane and dodecane formed from the washings and the polymer-bound $LiCuR_2$ indicated that about 50% of $LiCuR_2$ bound to PPh_2 and about 20% of the species bound to bpy leached irrespective of the polymer backbone. The bpy ligand thus provided better loading capacities than PPh_2 as evident from Table II. In the case of bpy ligand it is safe to consider it as a chelating ligand with Cu(I) attached to both N centers, and chelation appears to reduce the extent of leaching of the organocopper species.

Table II. Loading Capacities for $LiCuR_2$

polymer	ligand	capacity, mmol/g of support	method (eq)
	$LiCu(CH_3)_2$		
polystyrene (2% DVB)	PPh_2	1.2	1
		0.8	2
	bpy	1.7	1
		1.3	2
polyethylene	PPh_2	1.5	1
		1.0	2
	bpy	2.3	1
		2.0	2
polystyrene (soluble)	PPh_2	1.8	1
		1.0	2
	$LiCu(n\text{-}Bu)_2$		
polystyrene (2% DVB)	PPh_2	1.5	1
		1.1	2
	bpy	1.8	1
		1.2	2
polyethylene	PPh_2	1.6	1
		1.2	2
	bpy	2.6	1
		2.1	2
polystyrene (soluble)	PPh_2	1.6	1
		1.1	2

The stabilities of the polymers containing $LiCu(CH_3)_2$ and $LiCu(n\text{-}Bu)_2$ at room temperature were evaluated by keeping several 0.5-g batches of the polymers at room temperature under Ar and evaluating the amounts of $LiCuR_2$ intact at 24-h time intervals by reacting the polymer with 1-iodooctane. It was found that $LiCu(CH_3)_2$ bound to PPh_2 on polystyrene was stable for 4 days before a 10% reduction in the yield of nonane was observed. Further decomposition seemed to occur much more rapidly as the sample was more than 80% decomposed in 1 week. $LiCu(n\text{-}Bu)_2$ bound to PPh_2 on polystyrene was stable for 3 days before 10% decomposition was noticeable. These species appear to be more stable when bound to PPh_2 on polyethylene, $LiCu(CH_3)_2$ being stable for 6 days and $LiCu(n\text{-}Bu)_2$ being stable for 4 days before 10% decomposition occurred. By comparison the in situ prepared $LiCu(CH_3)_2$ and $LiCu(n\text{-}Bu)_2$ totally decomposed within a few hours at room temperature in the presence of PPh_3. These species bound to PPh_2 on polystyrene and polyethylene are stable for 3 weeks at 0 °C under Ar.

The stabilization of $LiCu(CH_3)_2$ and $LiCu(n\text{-}Bu)_2$ by bpy is interesting. It was reported earlier that bpy added to $LiCu(CH_3)_2$ and $LiCu(n\text{-}Bu)_2$ in solution did not significantly improve their stabilities even at lower temperatures.[11] We made a similar observation when bpy was added to in situ prepared species. However, bpy on the polymer dramatically improved the stabilities of both $LiCu(CH_3)_2$ and $LiCu(n\text{-}Bu)_2$. These species bound to bpy on polystyrene and polyethylene are stable for 2–3 weeks before a 10% decomposition is noticed. The slight variation in the period of stabilities is probably due to different amounts of oxygen leaking into these samples. Unlike the case of PPh_2 ligand, the stabilities of $LiCu(CH_3)_2$ and $LiCu(n\text{-}Bu)_2$ bound to bpy appear to be independent of the polymer backbone. Between the two ligands studied, bpy provides higher loading capacities and thermal stabilities for $LiCu(CH_3)_2$ and $LiCu(n\text{-}Bu)_2$. $LiCu(CH_3)_2$ bound to PPh_2 and bpy on polystyrene cross-linked with 2% DVB was also reacted with 2-cyclohexenone in thf at room temperature and was found to yield 3-methylcyclohexanone in 85–92% yield.

We have demonstrated that the organocopper compounds $LiCu(CH_3)_2$ and $LiCu(n\text{-}Bu)_2$ can be successfully immobilized on polymeric supports containing suitable coordinating ligands. The immobilized species can be isolated and stored at room temperature under Ar for up to several weeks without appreciable decomposition. We have also shown that significantly higher loading capacities for $LiCuR_2$ can be obtained by direct interaction of the polymer containing the stabilizing ligand with $LiCuR_2$ in solution compared to the reaction of polymer-bound CuI with LiR and that the leaching of the bound $LiCuR_2$ can be minimized using

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a chelating ligand as opposed to a monodentate ligand. The nature of the polymer backbone could be important, depending on the stabilizing ligand chosen. It is also possible to regenerate at least 40% of the original amount of $LiCuR_2$ on the polymer after it has been reacted with an organic substrate. Immobilizing organocopper compounds on polymeric supports bearing a suitable stabilizing ligand L has value despite the leaching problem as it ultimately affords organocopper species that have considerably longer lifetimes and can be reacted at higher temperatures than the in situ prepared species.

We are extending our studies to the reactions of the immobilized organocopper compounds to other organic substrates like α,β-unsaturated carbonyls, vinyl halides, and epoxides to demonstrate the stereospecific reactivities of the immobilized species. We are also investigating other stabilizing ligands in order to minimize the leaching problem and organocopper compounds to extend the usefulness of this procedure for their stabilization and isolation. Structural characterization of the immobilized species by infrared (4000–150 cm^{-1}) and multinuclear solid-state NMR spectroscopy are also in progress.

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Registry No. 1-Iodooctane, 629-27-6; nonane, 111-84-2; dodecane, 112-40-3.

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Synthesis and Characterization of Mo(nor)$_4$ (nor = 1-Norbornyl)

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There is a good possibility that dinitrogen binds to a Mo(IV) center in nitrogenase at some point during the process of being reduced to ammonia.[1] For this reason we have been interested in preparing monomeric d^2 complexes of the type MX_4 (M = Mo, W). We were encouraged that dinitrogen would bind to Mo(IV) or W(IV) by the fact that $[W(\eta^5\text{-}C_5Me_5)Me_3]_2(\mu\text{-}N_2)$, formally a dinitrogen complex with W(IV) at each end,[2] can be prepared in high yield by reducing $W(\eta^5\text{-}C_5Me_5)Me_3(CF_3SO_3)$ under N_2.[3] Although complexes of the type MX_4 where X is a bulky phenoxide (M = W)[4] or thiolate (M = Mo, W)[5] ligand have been prepared, none binds dinitrogen to any observable extent, perhaps in part because both alkoxide and thiolate[6] ligands are (to varying degrees) good π-electron donors. Therefore, we decided to explore MX_4 complexes in which X is an alkyl ligand. At least we might be able to use an MoR_4 species as a starting material for the preparation of monomeric molybdenum phenoxide complexes, still unknown species, in order to compare them with the analogous tungsten species.

MR_4 complexes where M = Mo or W are rare. η^3-Allyl[7] and benzyl[8] complexes are known for both Mo and W, but neither the allyl nor the benzyl ligand is likely to be unidentate. Mo(mesityl)$_4$[9] has been reported, although it was not characterized thoroughly, and so far we have not been able to reproduce the reported preparation. We felt that R should not be susceptible to decomposition reactions based on β- or α-hydrogen abstraction reactions,[10] a restriction that severely limits the possible choices of R.

In 1972 Bower and Tennent reported a series of tetra-1-norbornyl complexes containing first-row transition metals plus Zr and Hf.[11] Their stability was attributed to the fact that β elimination would produce a high-energy brigehead olefin. Cr(nor)$_4$ was reported to have a half-life of 7.6 h at 250 °C and to be stable indefinitely in 0.1 M H_2SO_4. It did not react with pyridine or several other small molecules. Since the ionic radius of molybdenum is ~0.12 Å larger than that of chromium, we thought it possible that the analogous Mo(nor)$_4$ complex might display greater reactivity toward small substrates. This note describes the synthesis and physical properties of Mo(nor)$_4$.

Experimental Section

All operations were performed under nitrogen in a Vacuum Atmospheres drybox or by standard Schlenk or vacuum-line techniques. All solvents were dried and freshly distilled under nitrogen prior to use. $MoCl_3(THF)_3$[12] and 1-norbornyllithium[13] were prepared according to literature procedures.

EPR spectra were recorded on a Varian E-Line spectrometer. Electrochemical measurements were performed by using a Princeton Applied Research Model 173 potentiostat/galvanostat and Model 175 universal programmer in conjunction with a Houston Instruments RE-0089 X-Y recorder. Cyclic voltammograms were obtained in the drybox in dichloromethane (dried and distilled) containing ~0.1 M $[n\text{-}Bu_4N]^+PF_6^-$. $E_{1/2}$ values are referenced to Ag/Ag^+ and uncorrected for junction potentials. Mass spectra were obtained on a Finnigan Mat 8200 spectrometer operating at low resolution. Magnetic susceptibility was determined in toluene-d_8 by the Evans technique.[14] A diamagnetic correction of -313.92×10^{-6} cgsu mol^{-1} was calculated using Pascals constants.[15] The mass susceptibility of toluene-d_8 was approximated by using the measured value for toluene-d_0 of -0.7176×10^{-6} cgsu g^{-1}.[16]

Preparation of Mo(nor)$_4$. $MoCl_3(THF)_3$ (2.0 g, 4.8 mmol) was added rapidly to a vigorously stirred solution of 1-norbornyllithium (1.95 g, 19.1 mmol) in 50 mL of a mixture of THF and ether (1:30 by volume) at −46 °C. As the reaction mixture was warmed to 25 °C, it became brown, then blue, and after ~90 min red with a blue precipitate. The reaction mixture was filtered to remove the bulk of the blue solids, and the solvent was removed from the filtrate in vacuo. The resulting red-brown residue was extracted with toluene, and the extract was filtered to remove any remaining blue solids. The volume of the red filtrate was then reduced in vacuo to yield crystals of red Mo(nor)$_4$. Two crops of red microcrystals totaling 550 mg (25%) were collected. Mo(nor)$_4$ can be purified further

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