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Preparation and reactivity of cyanocuprates containing alkylseleno and alkyltelluro groups as non-transferable ligands

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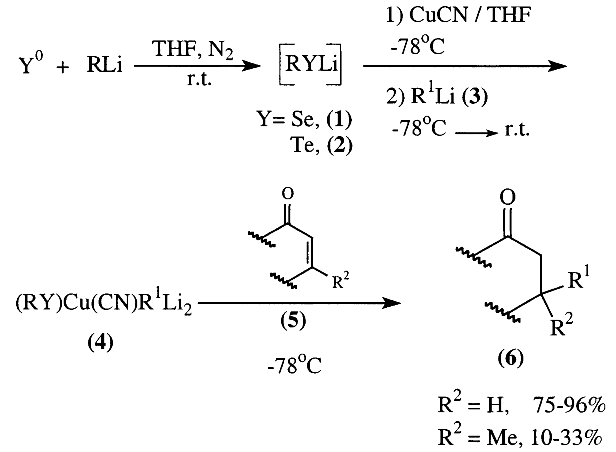
Abstract—Alkylseleno and alkyltelluro groups are efficient non-transferable ligands of cyanocuprates in 1,4-addition reactions to enones. © 2001 Published by Elsevier Science Ltd.

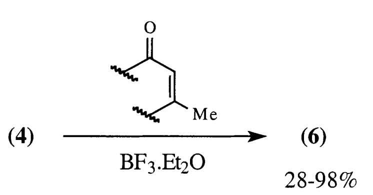
Non-transferable ligands play a crucial role in the reactivity and selectivity of a number of transformations using lower- or higher-order cuprates.[1] Several ligands have been used for this end.[2] The easy access to these ligands is decisive when a choice for one of them is to be made. Among the first non-transferable ligands to be used are the organothiolate groups.[3] In spite of the success of such ligands in organocopper chemistry, very few studies aiming to develop selenium analogs were reported.[4] To our knowledge, no mention of the use of organotellurolates as non-transferable ligands was made in the literature. In one of the studies concerning the use of phenylselenolate as ligands, Back and co-workers demonstrated that by changing the phenylthiolate group by the phenylselenolate in a lower-order cuprate, the selectivity in the transfer of the ligands was dramatically changed. MeCu(SPh)Li reacts with *E*-2-phenylseleno-1-(*p*-toluenesulfonyl)ethene transferring the PhS group, to give the β-thiovinylsulfone; the same *E*-selenovinylsulfone reacts with MeCu(SePh)Li to give the β-methylsulfone, by transfer of the methyl group.[4] In view of these facts, we decided to investigate systematically the use of alkylselenolate and alkyltellurolate anions as non-transferable ligands of cyanocuprates.[5]

Lithium alkylselenolate (**1**)[6] and alkyltellurolate (**2**)[7] are easily prepared by reacting elemental selenium or tellurium with commercial alkyllithiums at room temperature using tetrahydrofuran as the solvent. Reactions of **1** or **2** with CuCN, followed by the addition of a second equivalent of alkyllithium **3**, gives a clear solution presumably containing the cuprate **4**, which on reaction with enones **5** gives the 1,4-addition product **6** in good yields in the case of unhindered enones.[8] Hindered enones give poor yields of **6** (Scheme 1 and Table 1).

The R group can be the same as R^1 or it can be different. We observed no significant change in yields by using *n*-BuY instead of *s*-BuY or *t*-BuY (Y = Se, Te) as the non-transferable ligand. In view of this fact, the *n*-BuY groups are the ligands of choice due to easier manipulation and lower cost of *n*-BuLi.



Scheme 1.



Scheme 2.

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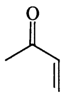
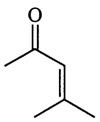
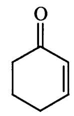
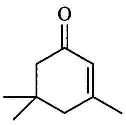
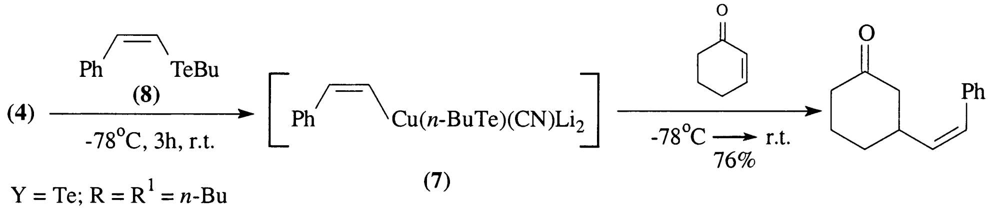
Table 1. Yields of the 1,4-addition reactions to enones using RY (Y = Se, Te) as non-transferable ligands

									
R	R^1	a	b	a	b	a	b	a	b
n-Bu	*n*-Bu	90	76	32	30	96	86	33	31
				(89)	(98)			(87)	(68)
								(90^d)	(96^d)
s-Bu	*s*-Bu	96	89	33	31	75	95	33	30
				(76)	(98)			(59)	(78)
n-Bu	*s*-Bu	90	94	-	-	93	95	-	-
				(75)	(63)			(83)	(58)
t-Bu	*t*-Bu	90	86	10	11	90	85	10	11
				(40)	(35)			(45)	(28)
n-Bu	*t*-Bu	89	93	-	-	83	80	-	-
				(39)	(36)			(30)	(38)
								(41^d)	(42^d)

^{a}Y = Se; ^{b}Y = Te; ^{c}yields in parenthesis refer to the reaction in the presence of $BF_3.Et_2O$; ^{d} yields of the reaction using Me_3SiCl.



Scheme 3.

The yields of the 1,4-addition to hindered enones were improved by using $BF_3{\cdot}Et_2O$ as an additive, as shown in Scheme 2 and Table 1.[9] Me_3SiCl is also effective to promote the 1,4-addition to hindered enones, as shown in Table 1 for the reaction of isophorone with four representative cuprates.

In only one case, when the group to be transferred was *t*-Bu, the yields were low. In all cases studied no transfer of the alkylseleno and alkyltelluro groups to enones was observed.

Cuprates **4** can be used to generate vinylic cyanocuprates **7** by transmetallation with vinylic tellurides **8** (Scheme 3).

In conclusion, we showed that the easily prepared lithium alkylselenolates and tellurolates are efficient non-transferable ligands for cyanocuprates in the reaction with enones.

Acknowledgements

The authors thank FAPESP and CNPq for support.

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8. Typical procedure: In a two-necked 50 mL flask under nitrogen and magnetic stirring was placed elemental tellurium (511 mg, 4 mmol) in dry THF (5 mL). To this suspension at room temperature was added *n*-butyllithium (3.08 mL of a 1.3 M solution in hexane, 4 mmol). A yellow solution formed. This solution was transferred via cannula to a second two-necked 50 mL flask under nitrogen and magnetic stirring containing a suspension of CuCN (358 mg, 4 mmol) in THF (5 mL) at −78°C. The mixture was kept at this temperature for 15 minutes and then *t*-butyllithium (6.15 mL of a 0.65 M solution in hexane, 4 mmol) was added. The cooling bath was removed and the mixture was stirred until a clear solution formed. Then it was cooled again to −78°C and cyclohexenone (370 mg, 3.8 mmol) was added. The mixture was allowed to reach the room temperature and maintained under stirring for 1 h. A dark precipitate formed. The organic phase was diluted with NH_4Cl/NH_4OH (3:1, 5 mL) and then with a 10% solution of sodium hypochlorite (3×10 mL). The organic phase was further washed with NH_4Cl/NH_4OH solution until the blue color of the aqueous phase disappeared. The organic phase was dried with magnesium sulfate and the solvent was evaporated. The residue was distilled in a Kugelrohr oven under vacuum. Yield of 3-*tert*-butylcyclohexanone: 490 mg (83%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 0.92 (s, 9H), 1.21–1.23 (m, 1H), 1.41–1.62 (m, 2H), 1.82–2.21 (m, 4H), 2.3–2.48 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 25.61, 26.17, 27.14, 32.68, 41.27, 43.61, 49.35, 212.60; LRMS m/z (relative intensity, %): 154.2 (M^+, 16%), 139.2 (3%), 121.2 (3%), 98.2 (97%), 83 (42%), 57 (100%).
9. Typical procedure for the reaction using $BF_3 \cdot Et_2O$: The same procedure described above for the preparation of the cyanocuprate **4** was followed. Then $BF_3 \cdot Et_2O$ (1.49 mL, 12 mmol) was added slowly at −78°C and the mixture was kept at this temperature for 15 minutes, giving an orange solution. Isophorone (498 mg, 3.6 mmol) was then added and the mixture was stirred for 3 h at room temperature. The work-up was identical to the one described above. Yield of 3,5,5-trimethyl-3-butylcyclohexanone: 610 mg (87%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 0.88 (t, $J=7.2$ Hz, 3H), 0.98 (s, 3H), 1.02 (s, 3H), 1.03 (s, 3H), 1.19–1.28 (m, 6H), 1.45–1.63 (m, 2H), 2.06–2.18 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 14.20, 23.53, 26.21, 27.72, 30.93, 32.48, 36.15, 38.83, 44.79, 49.36, 53.32, 54.47, 213.10; LRMS m/z (relative intensity, %): 181.3 (1%), 139.3 (32%), 111.2 (3%), 97.2 (28%), 83.2 (100%), 55.0 (44%).