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Ni(II)- AND Co(II)-PHOSPHINE COMPLEX CATALYZED CARBON-CARBON BOND FORMATION BETWEEN ORGANIC TELLURIDES AND GRIGNARD REAGENTS[1]

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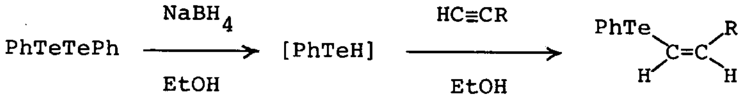
Summary: Treatment of alkenyl and aryl tellurides with Grignard reagents in the presence of $NiCl_2(PPh_3)_2$, $NiCl_2(Ph_2PCH_2CH_2CH_2PPh_2)$, or $CoCl_2(PPh_3)_2$ as catalyst affords the cross-coupling products together with the homo-coupling products of the tellurides in good to moderate yields under mild conditions.

Recently, much attention are focused on preparation of new organotellurium compounds and their utilization for organic synthesis,[2-4] and yet a useful carbon-carbon bond formation using those seems to be very limited to date.[5-8] We communicate here a first example of nickel(II)- and cobalt(II)-phophine complex catalyzed facile cross-coupling between Grignard reagents and easily accessible organic tellurides.[9]

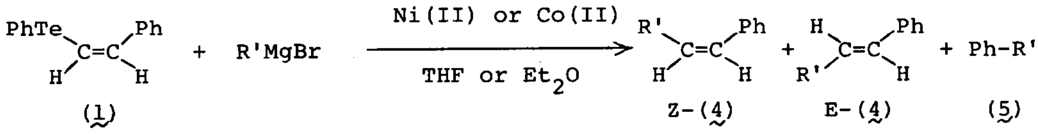
First we prepared several alkenyl tellurides [(1)-(3)] in 70-100% yields by completely regiospecific and trans-stereospecific addition of phenyltellurol, prepared in situ by reduction of diphenyl ditelluride with sodium borohydride, to the corresponding acetylenes(Scheme 1).[10] When (1)(1 equiv.) was treated with phenylmagnesium bromide(2.5 equiv.) in the presence of a catalytic amount of $NiCl_2(PPh_3)_2$ in tetrahydrofuran(THF) at 20°C for 10 min under nitrogen atmosphere, stilbene [Z- and E-(4; R'=Ph), 60% yield, Z/E=9/1] and biphenyl [(5; R'=Ph), 92%



(1): R=Ph
(2): $R=CO_2Et$
(3): $R=CH_2OH$

Scheme 1

yield] were obtained as products(Scheme 2). Tellurium was deposited as a black metal. A similar reaction at reflux temperature for 3 h improved both the yield



Scheme 2

and cis-selectivity of stilbene (100% yield, Z/E=98/2). The result shows that a formal substitution of PhTe moiety by Ph group occurred mainly retentively. The corresponding cobalt(II) catalyst and $NiCl_2$(dppp)[11] were revealed to be also effective, although either cis-selectivity or the yield of stilbene was slightly lower. The reaction of (1) with alkylmagnesium bromide gave much lower yields of the corresponding (4) and (5) in either THF or diethyl ether. Typical results are shown in Table 1.

Application of the reaction to diaryl telluride resulted in the formation of the expected corresponding cross- and homo-coupling products with the organic moiety of Grignard reagnet selectively replacing the tellurium group at ipso-position(Scheme 3 and Table 2). All these coupling reactions did not proceed at

$$\underset{(6)}{Ar_2Te} + RMgBr \xrightarrow[\text{THF or } Et_2O]{\text{Ni(II) or Co(II)}} \underset{(7)}{Ar\text{-}R} + \underset{(8)}{Ar\text{-}Ar} + \underset{(9)}{R\text{-}R}$$

Scheme 3

all in the absence of Ni(II)- or Co(II)-phosphine complex, and no products were obtained when the reaction was carried out only with organic tellurides and phosphine complex.

By considering the proposed mechanism for the Ni(II)-phosphine complex catalyzed cross-coupling between organic halides and Grignard reagent[12] and the fact that tellurium metal was deposited through the reaction, the reaction seems to involve the following steps: 1) Formation of diorganonickel or -cobalt complex, 2) Subsequent conversion by organic telluride to aryltelluro(organo)nickel or -cobalt complex, and 3) Elimination of tellurium, followed by reductive elimination to give the products. More details will be presented in a full account.

Table 1. Ni(II)- and Co(II)-phosphine complex catalyzed formation of (**4**) and (**5**) from (**1**) and Grignard reagent.a)

R'	Catalyst b)	Solvent	Temp.(°C)	Time(h)	Yield(mmol) c)		
(2.5 mmol)	(0.05 mmol)	(10 ml)			(**4**)	(Z:E)	(**5**)
Ph	A	THF	20	0.17	0.60	(90:10)	0.92 d)
Ph	A	THF	20	5	0.81	(97:3)	0.99 d)
Ph	A	THF	67	3	1.00	(98:2)	1.36 d)
Ph	B	THF	20	5	0.53	(100:0)	0.48 d)
Ph	C	THF	20	5	1.00	(90:10)	1.04 d)
n-Bu	A	Et_2O	35	5	0.11	(85:15)	0.06 e)
n-Bu	B	Et_2O	35	5	0.22	(80:20)	0.17 e)
n-Bu	C	Et_2O	35	5	0.12	(85:15)	0.04 e)

a) Carried out using (**1**) (1 mmol) under N_2. b) A: $NiCl_2(PPh_3)_2$. B: $NiCl_2$-(dppp). C: $CoCl_2(PPh_3)_2$. c) Determined by GLC. d) This was produced by cross-coupling as well as homo-coupling of PhMgBr. e) A small amount of n-octane was also formed, but not determined.

Table 2. Ni(II)- and Co(II)-phosphine complex catalyzed cross- and homo-coupling of diaryl telluride with Grignard reagent.a)

(**6**) Ar	R	Catalyst b)	Solvent	Temp.	Time	Yield(mmol) c)		
(1 mmol)	(2.5 mmol)	(0.05 mmol)	(10 ml)	(°C)	(h)	(**7**)	(**8**)	(**9**)
p-$MeOC_6H_4$	Ph	A	THF	20	5	0.97	0.22	0.54
p-$MeOC_6H_4$	Ph	C	THF	20	5	0.31	0.06	0.42
H	p-$MeOC_6H_4$	A	THF	20	5	0.78	0.18	0.29
H	n-C_6H_{13}	A	Et_2O	35	8	0.12	0.33	0.75
H	n-C_6H_{13}	B	Et_2O	35	8	0.44	0.33	0.24

a) Carried out under N_2. b) See a footnote of Table 1. c) Determined by GLC.

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References and Notes

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10. At reflux for a few minutes for reduction and for 20 h for addition. (1): R=Ph, yellow solid, m.p. 43-44°C(from EtOH), ^{1}H-NMR(220 MHz), δ, 7.07(1H, d, J=11Hz), 7.15-7.35(8H, m), 7.45(1H, d, J=11Hz), 7.73(2H, d, J=7Hz). (1): R=CO$_2$Et, orange oil, ^{1}H-NMR(100 MHz), δ, 6.94(1H, d, J=10Hz), 8.48(1H, d, J=10 Hz). (1): R=CH$_2$OH, orange oil, ^{1}H-NMR(100 MHz), δ, 6.52(1H, dt, J=10 & 5Hz), 6.92(1H, dt, J=10 & 1.5Hz). Cf. S. R. Buzilova, I. D. Sadekov, T. V. Lipovich, T. M. Filippova, and L. I. Vereshchagin, Chem. Abstr., 88, 22289v(1978).
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