Nickel(0) complex-catalysed detelluration of diorganyl tellurides and ditellurides with phosphines

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Nickel(0) complexes efficiently catalyse detelluration of diaryl tellurides and diaryl ditellurides in the presence of phosphines to afford biaryls in high yields.

Organotellurium compounds are becoming increasingly important in organic synthesis.[1] As reported by Bergman *et al.* more than two decades ago,[2] aryltelluriums undergo detelluration upon treatment with degassed Raney nickel to afford biaryls. The high accessibility of the aryltelluriums[1,2] has made the detelluration a convenient method for the synthesis of biaryls. However, attempted transition metal-catalysed detelluration has been unsuccessful to data.[2,3] Hence, although the reaction is interesting and synthetically useful, the necessity of more than a stoichiometric amount of the metal is still a serious drawback. Herein reported are (*i*) highly successful nickel-catalysed detelluration of diaryl tellurides with phosphines affording biaryls and (*ii*) its mechanism involving an unexpected disproportionation of the complexes formed by oxidative addition of C–Te bonds to $Ni(PEt_3)_4$.[4]

Heating a mixture of dianisyl telluride (**1a**, 684 mg, 2 mmol) and $Ni(PEt_3)_4$ (106 mg, 10 mol% relative to **1a**) in benzene (4 ml) at 80 °C slowly formed black precipitates to give the detelluration product 4,4′-bianisyl **2a** in 13% GC yield after 20 h.† Prolonged heating did not improve the yield, indicating a very poor turnover of the complex catalyst. However, a higher turnover was achieved when a free phosphine was added to the reaction system [eqn. (1)]. Thus, the yield of **2a** increased to 30% and further to 65% when the reaction was conducted under the same conditions in the presence of 1.2 and 3.0 equiv. (relative to **1a**) of free PEt_3, respectively (Table 1). Although reactions in acetonitrile gave slightly higher yields than those in benzene, the difference was marginal. The effect of the concentration of **1a** on the yield was not significant either at concentrations ranging from 0.8 to 2 mmol of **1a** in 4 ml of the solvent. However, the nature of the phosphine employed exerted a decisive effect. PBu_3 was as effective as PEt_3, but the use of more sterically demanding or less electron-donating phosphines such as PPr^i_3 and $PMePh_2$ reduced the yield. As compared to these triorganophosphines, however, aminophosphines proved much more efficient to achieve significant improvement in the product yield. In the presence of 1.2 equiv. of $P(pyrro)_3$ (pyrro = pyrrolidinyl), for example, starting telluride **1a** disappeared completely after 20 h (80 °C) to afford **2a** quantitatively. Note that a yield as high as 95% was obtained even when the amount of the nickel catalyst was reduced to 3 mol%. Obviously, the yield of **2a** increases in the order $PMePh_2 < PEt_3 \approx PBu_3 < P(NEt_2)_3 < P(pip)_3$ (pip = piperidinyl) < $P(pyrro)_3$. The trend is in good agreement with the reactivity of phosphines toward tellurium to form phosphine tellurides ($Te{=}PR_3$), $P(pyrro)_3$ being most reactive.[5]‡

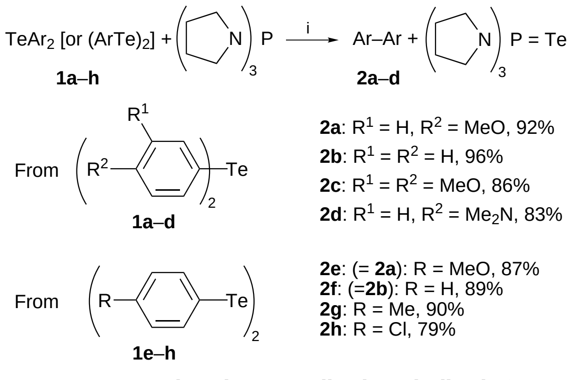
$$\underset{\mathbf{1a}}{Te(C_6H_4OMe\text{-}4)_2} + PR_3 \xrightarrow[80\ °C,\ 20\ h]{Ni(PEt_3)_4\ (10\ mol\%)} \underset{\mathbf{2a}}{(4\text{-}MeOC_6H_4)_2} + Te{=}PR_3 \quad (1)$$

The Ni-catalysed detelluration could be readily applied to other diaryl tellurides affording the corresponding biaryls in good yields (Scheme 1).§ Besides methoxy group, the amino functionality was also tolerant towards the reaction, and a good yield of the corresponding product was obtained. Moreover, the new procedure could be successfully applied to diaryl ditellurides. Thus, the reactions of $(PhTe)_2$ and $(4\text{-}MeOC_6H_4Te)_2$ with 2.5 equiv. of $P(pyrro)_3$ catalysed by $Ni(PEt_3)_4$ (10 mol%) in acetonitrile under similar conditions readily afforded high yields of the corresponding biaryls in both cases. The reaction of $(4\text{-}ClC_6H_4Te)_2$ was particularly noticeable; 4,4′-dichlorobiphenyl was selectively formed in 79% yield despite the potential reactivity of chloroarenes toward Ni^0 species. Since diaryl ditellurides are more readily synthesized then tellurides, successful application of the procedure to ditellurides significantly expands the scope of the reaction.

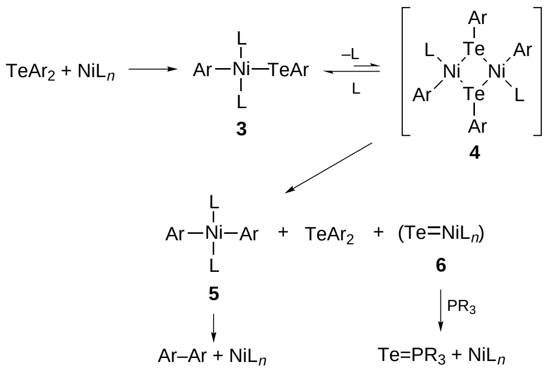
Table 1 Detelluration of dianisyl telluride **1a** catalysed by $Ni(PEt_3)_4$[a]

Run	Solvent/quantity of **1a** (mmol)/ additive (equiv. relative to **1a**)	GC yield of **2a** (%)
1	C_6H_6/2/none	13
2	C_6H_6/2/PEt_3 (1.2)	30
3	C_6H_6/2/PEt_3 (3.0)	65
4	MeCN/2/PEt_3 (1.2)	41
5	MeCN/0.8/PEt_3 (1.2)	42
6	MeCN/2/PEt_3 (3.0)	73
7	MeCN/1.2/PEt_3 (5.0)	93
8	MeCN/2/PBu_3 (1.2)	40
9	MeCN/0.8/$Pi\text{-}Pr_3$ (1.2)	29
10	MeCN/0.8/$PMePh_2$ (1.2)	20
11	MeCN/0.8/$P(NEt_2)_3$ (1.2)	41
12	MeCN/0.8/$P(pip)_3$ (1.2)[b]	56
13	MeCN/0.8/$P(pyrro)_3$ (1.2)[b]	*ca.* 100
14	MeCN/0.8/$P(pyrro)_3$ (0.5)[b]	70
15	MeCN/0.8/$P(pyrro)_3$ (1.2)[b]	95[c]
16	MeCN/0.8/$P(pyrro)_3$ (1.2)[b]	61[d]

[a] All reactions were run in a Schlenk flask under argon atmosphere at 80 °C for 20 h, using 10 mol% of $Ni(PEt_3)_4$ and 4 ml of a solvent. Yields of **2a** were determined by GC using biphenyl as an internal standard. [b] pip = Piperidinyl; pyrro = pyrrolidinyl. [c] 3 mol% $Ni(PEt_3)_4$ was used. [d] 3 mol% $Ni(PPh_3)_4$ was used as the catalyst.

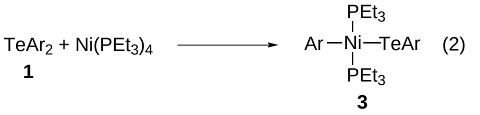


Scheme 1 *Reagents and conditions*: i, telluride or ditelluride (2.0 mmol), $Ni(PEt_3)_4$ (10 mol%), $P(pyrro)_3$ (2.4 or 5.0 mmol for telluride or ditelluride respectively), MeCN, 80 °C, overnight



Scheme 2

The detelluration of tellurides is likely to proceed, as depicted in Scheme 2, *via* oxidative addition of a telluride to the nickel complex, disproportionation of the resulting complex **3** to generate diarylnickel species **5**, and its reductive elimination. The mechanism is substantiated by the following observations. As previously reported,[4] treatment of $TePh_2$ (340 mg, 1.206 mmol) with $Ni(PEt_3)_4$ (427 mg, 0.804 mmol) in C_6D_6 at room temp. gave complex **3b** in 10 min, which displayed a singlet at δ 10.3 in its ^{31}P NMR spectrum [eqn. (2)]. Complex **3b** was liquid and rather unstable so prohibiting further purification. Telluride **1a** also reacted similarly to form oily complex **3a**. However, oxidative addition of $Te[C_6H_3(OMe)_2\text{-}3,4]_2$ **1c** with the nickel complex gave analytically pure complex **3c** (87% yield) as a black solid.¶



$$\mathrm{TeAr_2 + Ni(PEt_3)_4 \longrightarrow Ar{-}\overset{PEt_3}{\underset{PEt_3}{Ni}}{-}TeAr} \qquad (2)$$

1 **3**

a, Ar = C_6H_4OMe-4; **b**, Ar = Ph; **c**, Ar = $C_6H_3(OMe)_2$-3,4

These nickel complexes **3** gradually decomposed even at room temp. For example, NMR spectroscopy revealed that the spontaneous decomposition of **3b** in C_6D_6 resulted in precipitation of a black solid (presumably a nickel telluride like **6**) to generate *trans*-$NiPh_2(PEt_3)_2$ **5b**[6] and $TePh_2$ (approximately 1 : 1 ratio; the conversion of **3b** was *ca.* 50% after 2 d) in solution. A very similar decomposition process was observed with complex **3c**, where the diarylnickel complex **5c** and the telluride **1c** were found by ^1H and ^{31}P NMR spectroscopy to be formed in addition to the black precipitates. As expected, the decomposition was faster at elevated temperatures. Thus, while only *ca.* 50% of complex **3c** decomposed at room temp. over 10 h, it disappeared completely within 3 h at 50 °C to afford **5c** and **1c** in *ca.* 1 : 1 ratio, which accounted for over 93% of the total aryl groups as estimated by ^1H NMR spectroscopy. Heating to even higher temperatures induced a secondary decomposition (reductive elimination); diarylnickel complex **5c** generated *in situ* through the decomposition of **3c** at 50 °C in a sealed NMR tube disappeared after overnight heating at 100 °C and the corresponding biaryl was obtained in 91% NMR yield (based on the quantity of **1c**). This reductive elimination process obviously results in regeneration of Ni^0 species, which carries the catalysis. Interaction of **6** with a phosphine molecule forming a phosphine telluride presumably is another route to the Ni^0 species. Further mechanistic detail of the decomposition of **3** leading to the generation of **5** is ambiguous at the moment. It may involve a dimeric intermediate such as **4** (Scheme 2), palladium analogues of which have been proposed.[7] A supportive observation was made in a catalytic reaction [1.2 equiv. $P(pyrro)_3$, 3 mol% $Ni(PEt_3)_4$, acetonitrile, 80 °C, 10 h] of an unsymmetrical telluride, $TeAr^1Ar^2$ ($Ar^1 = C_6H_4NMe_2$-4, $Ar^2 = C_6H_4OMe$-4), which gave not only Ar^1–Ar^2 but also cross-over products, Ar^1–Ar^1 and Ar^2–Ar^2 (Ar^1–Ar^1 : Ar^1–Ar^2 : Ar^2–Ar^2 = 1 : 3 : 1) in 73% total yield. The telluride recovered in *ca.* 10% was also a mixture of $TeAr^1_2$, $TeAr^1Ar^2$ and $TeAr^2_2$.

Further synthetic application of the facile oxidative addition of C–Te bonds to Ni, Pd and Pt complexes[4] is now under extensive study.

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Footnotes and References

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† Most of **1a** (83% based on GC) remained unreacted. In the absence of the nickel catalyst, no coupling product was formed under similar conditions, indicating that the nickel catalyst was essential for the reaction.

‡ Formation of Te=$P(pyrro)_3$ in the detelluration reaction with $P(pyrro)_3$ was confirmed by ^{31}P NMR. See ref. 5.

§ *Typical experimental procedure:* A mixture of telluride **1a** (684 mg, 2 mmol), $P(pyrro)_3$ (579 mg, 2.4 mmol) and $Ni(PEt_3)_4$ (106 mg, 0.2 mmol) in acetonitrile (5 ml) was heated at 80 °C overnight (20 h). The reaction mixture was poured into 10 ml of 1 M HCl to liberate metallic tellurium instantly. Extraction using CH_2Cl_2, drying over $MgSO_4$ and concentration afforded crude **2a**, which was subsequently passed through a short silica gel column (ethyl acetate–chloroform–hexane = 0.5 : 1 : 8) to give pure product **2a** as a white solid (394 mg, 1.84 mmol, 92%).

¶ A mixture of **1c** (371 mg, 0.923 mmol) and $Ni(PEt_3)_4$ (500 mg, 0.941 mmol) in benzene (6 ml) was stirred at room temp. for 15 min. Concentration of the reaction mixture to *ca.* 0.5 ml resulted in the precipitation of analytically pure complex **3c** as a black solid in 87% yield (560 mg, 0.803 mmol). *Selected data* for **3c**: ^1H NMR (300 MHz, C_6D_6) δ 7.78 (d, 1 H, *J* 8.0 Hz), 7.67 (s, 1 H), 7.11 (s, 1 H), 6.89 (d, 1 H, *J* 7.8 Hz), 6.66 (d, 1 H, *J* 7.8 Hz), 6.41 (d, 1 H, *J* 8.0 Hz), 3.67 (s, 3 H), 3.52 (s, 3 H), 3.50 (s, 3 H), 3.40 (s, 3 H), 1.34–1.42 (m, 12 H), 0.90–1.09 (m, 18 H); ^{31}P (121.5 MHz, C_6D_6) δ 11.3. Anal. Calc. for $C_{28}H_{48}NiO_4P_2Te$: C, 48.26; H, 6.94. Found: C, 48.21; H, 7.07%.

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