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Prospective

Recent approach to incorporate tellurium in metal carbonyl cluster utilizing extrusion reaction

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Abstract

The incorporation of tellurium into metal carbonyl using tellurium transfer/ extrusion reaction is presented in this work. The results bring one of the new ways to incorporate tellurium by transferring it from one molecule to another molecule, in comparison to the work so far where either insertion or extrusion reactions were shown. The reactions of PhC_2TeC_2Ph with the metal carbonyl cluster produced thermodynamically stable metal carbonyl tellurium clusters.

More Information

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Tellurium based compounds can be formed or modified by two types of reactions which are insertion and extrusion reactions [1]. With reference to the tellurium based reactions, the chemical reactions where tellurium, connected to two other atoms A and B, is lost to form an A-B bonded molecule are the extrusion reactions as shown in equation 1.

$$A - Te - B \xrightarrow{-Te} A - B \qquad \text{eq. 1}$$

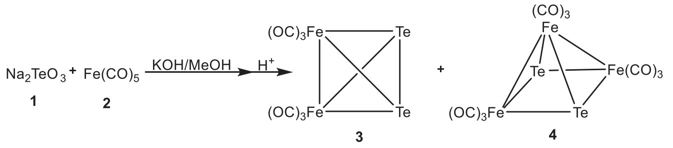
Insertion reactions are the reverse chemical process where tellurium gets inserted between A and B, to form A-B molecule, as shown in equation 2.

$$A - B \xrightarrow{+Te} A - Te - B \qquad \text{eq. 2}$$

We introduced one more equation here, in which a reaction of A-Te-B, with C-D forms A-B and C-Te-D by tellurium transfer reaction, as shown in equation 3.

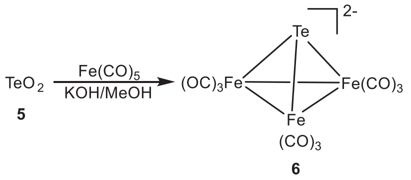
$$A - Te - B + C - D \xrightarrow{-Te/+Te} A - B + C - Te - D \qquad \text{eq. 3}$$

Initially, the synthesis of square-pyramidal triiron clusters $[Fe_3Te_2(CO)_9]$ (3) was carried by Hieber process by reacting Na_2TeO_3(1) with $Fe(CO)_5$ (2) in basic methanol solutions, followed by acidification (Scheme 1) [2].



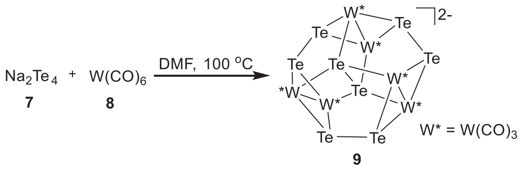
Scheme 1

Later the method was modified, and the tellurium and TeO_2 were directly used as the source for the synthesis of 16-transition metal carbonyl clusters. In the iron cluster system, TeO_2 reaction with iron carbonyl in basic conditions yielded tetrahedral clusters $[TeFe_3(CO)_9]^{2-}$ (6) (Scheme 2) [3].

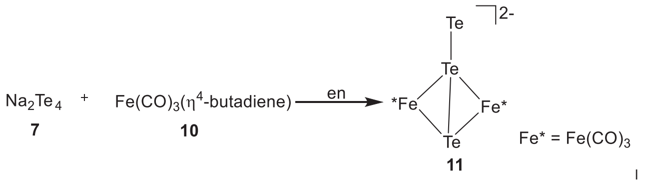


Scheme 2

Another approach was to use the Zintl ions with metal carbonyls where reductive attack of polychalcogenides on the metal atoms followed by oxidative decarbonylation produced different high nuclearity carbonyl cluster. For example, $[(Te_2)_4W_6(CO)_{18}]^{2-}$ (9) was formed by the reaction of Na_2Te_4 (7) and $W(CO)_6$ (8) at 100 °C in DMF solution (Scheme 3). Similarly, $Fe(CO)_3$(4-butadiene) (10) reaction with Na_2Te_4 produced the butterfly $[(Te)Te_2Fe_2(CO)_6]^{2-}$ (11) (Scheme 4) [4].

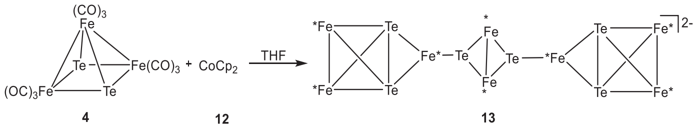


Scheme 3



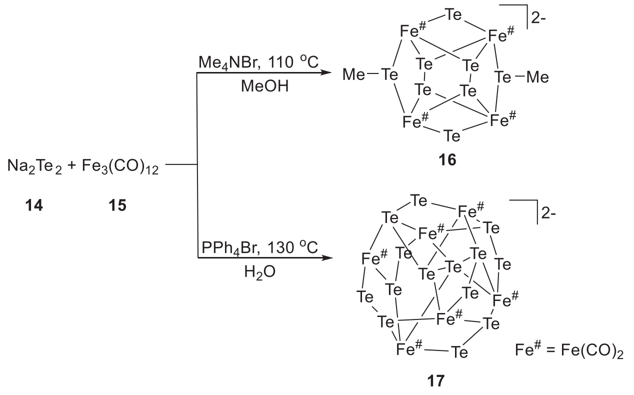
Scheme 4

Another approach showed that the reduction of the iron clusters say triiron telluride cluster $[Fe_3Te_2(CO)_9]$ (4) with 2 equiv. of $CoCp_2$ (12) produced larger di-Te_2Fe_3 cluster which was $[Te_6Fe_8(CO)_{24}]^{2-}$ (13) (Scheme 5) [5,6].



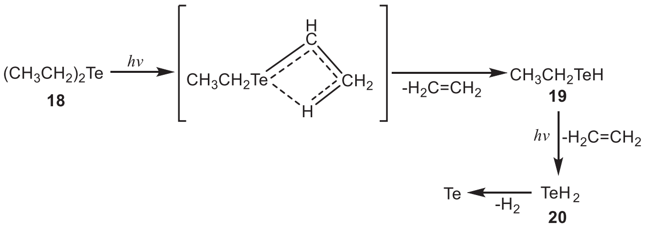
Scheme 5

Other method includes hydro(solvo)thermal conditions by the use of which the oxidative decarbonylation of trinuclear iron cluster took place, for example, $Fe_3(CO)_{12}$ (15) reaction with Na_2Te_2 (14) in MeOH at 110 °C or water at 130 °C gave the poly-ditelluride-iron clusters which were $[(TeMe)_2(Te)_2(Te_2)_2Fe_4(CO)_8]^{2-}$(16) and $[(Te_2)_7Fe_6(CO)_{12}]^{2-}$ (17), respectively (Scheme 6) [7].



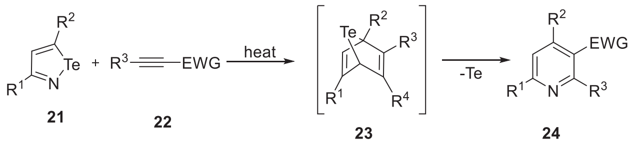
Scheme 6

The second type of reaction was extrusion reaction where the stepwise cleavage of carbon-tellurium bond took place with the extrusion, which produced different products along with the liberation of tellurium (Scheme 7) [8]. This extrusion can be brought about by thermal treatment or Laser-induced photolysis of 18.



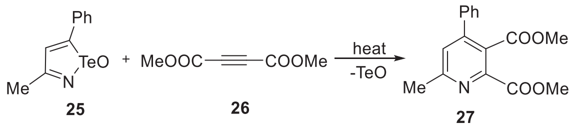
Scheme 7

Isotellurazoles (21) exclude tellurium after the addition of acetylenic dienophiles (22) to produce the polysubstituted pyridines (24) (Scheme 8) [9].



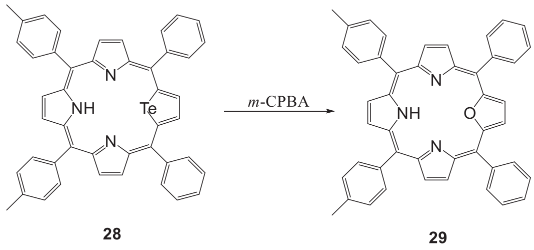
Scheme 8

It was found that this reaction can only be favourable when at least one substituent on the acetylene was electron withdrawing [9]. Similarly, isotellurazole Te oxides (25) extrudes TeO and Te to form substituted pyridines (27) (Scheme 9) [9].



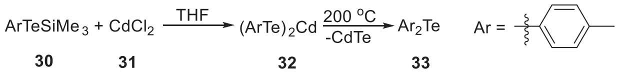
Scheme 9

In another case, replacement of the tellurium atom by oxygen to form 29 was found in the peracid environment in the oxidation of a tellurophene (28) (Scheme 10) [10].



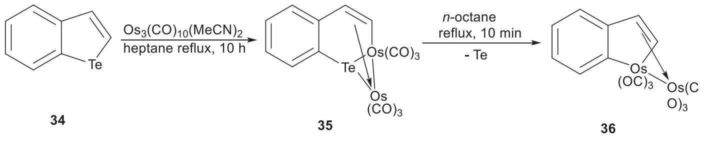
Scheme 10

Other examples include the extrusion of tellurium from Bis-aryltelluro-cadmium (30) and Bis-aryltelluro-mercury compounds (Scheme 11) [11].



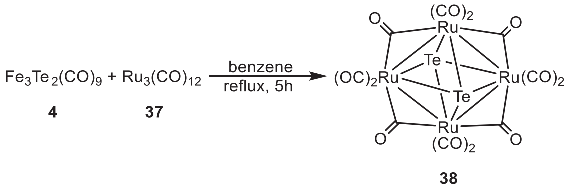
Scheme 11

And, trinuclear metal carbonyl clusters on reaction with benzo[*b*]tellurophene (34) at higher temperatures afforded product with the expansion in the ring (35) (Scheme 12) [12].



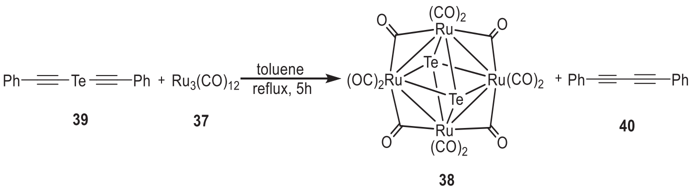
Scheme 12

In the above examples, we did not notice that the extruded tellurium atom is utilised by the other reactant, or moieties present in the same reaction medium. We introduce a third type or another type of extrusion reaction called tellurium transfer/ extrusion reaction. To support this another kind of reaction, we found the examples where the extruded tellurium atom is utilised by the other simple metal carbonyl present in the reaction medium to produce the metal clusters incorporated with tellurium. Our previous paper presented an interesting $Ru_4Te_2(CO)_{12}$ cluster example which was synthesised, by the reaction of $Fe_3Te_2(CO)_9$ and $Ru_3(CO)_{12}$ in benzene for 5h at reflux (Scheme 13) [13].



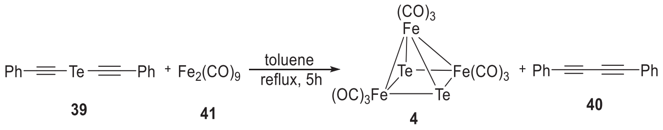
Scheme 13

Same $Ru_4Te_2(CO)_{12}$ product can be obtained in 40% yield (based on $Ru_3(CO)_{12}$), by the reaction of PhC_2TeC_2Ph with $Ru_3(CO)_{12}$ along with PhC_2C_2Ph (76% yield), which shows the transfer of tellurium from PhC_2TeC_2Ph to $Ru_4Te_2(CO)_{12}$ (Scheme 14).



Scheme 14

Further, we performed other reaction of $Fe_2(CO)_9$ with PhC_2TeC_2Ph in thermal reaction conditions and found the earlier synthesised stable $Fe_3Te_2(CO)_9$ (4) cluster [2] as the product (45% yield based on $Fe_2(CO)_9$) with the liberation of PhC_2C_2Ph (85% yield) (Scheme 15).



Scheme 15

Conclusion

We believe and propose that the reaction of PhC_2TeC_2Ph with the metal carbonyl cluster will produce the more thermodynamically stable metal carbonyl tellurium clusters in thermal reaction conditions [14].

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Electronic Supplementary Information

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