Transalkynylation and catalytic demercuration of bis(alkynyl)mercurials: two alternative mechanisms

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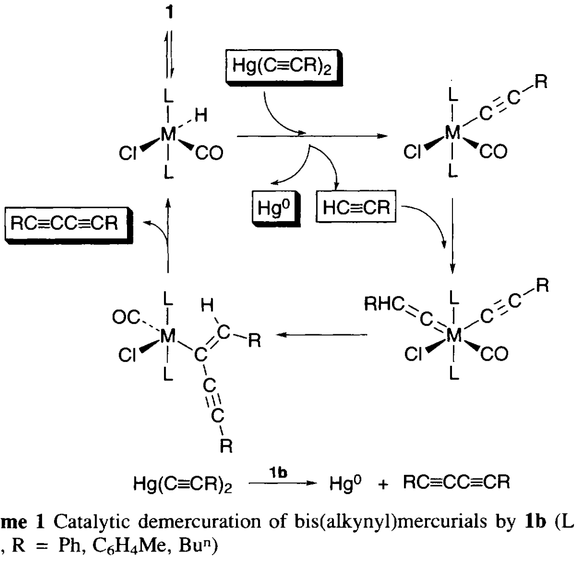
The complexes [RhCl(CO)(PPh$_3$)$_2$] and [MHCl(CO)(PPh$_3$)$_3$] (M = Ru, Os) catalyse the demercuration of [Hg(C≡CR)$_2$] (R = Ph, C$_6$H$_4$Me-4, Bu^n) to provide buta-1,3-diynes, however the reactions proceed by quite different mechanisms as indicated by (*i*) the isolation of [Ru{C(C≡CR)=CHR}Cl(CO)(PPh$_3$)$_2$] and its reintroduction into the catalytic cycle and (*ii*) the isolation of the iridium complex [IrCl(C≡CR)(HgC≡CR)-(CO)(PPh$_3$)$_2$].

The coupling of terminal alkynes by copper salts has long been established and remains the preferred route for the formation of symmetrical buta-1,3-diynes.[1] Bis(alkynyl)mercurials, [Hg(C≡CR)$_2$] emerged early as convenient crystalline derivatives for the characterisation of terminal alkynes[2] although their deployment as alkynyl transfer reagents has not been extensively studied. We have described unsuccessful[3] attempts to use these reagents for the mild transfer of alkynyl groups to transition metals, in particular ruthenium.[4] Our unsuccessful efforts led to the development of a convenient route to 3-en-1-yn-3-yl complexes of ruthenium, [Ru{C(=CHR)C≡CR}-Cl(CO)(PPh$_3$)$_2$] [R = Ph **2a**, C$_6$H$_4$Me **2b**, Bu^n **2c**] *via* the reaction of [RuHCl(CO)(PPh$_3$)$_3$] **1a** with [Hg(C≡CR)$_2$] (Scheme 1)[3] however we find that this route fails for the corresponding osmium complex [OsHCl(CO)(PPh$_3$)$_3$] **1b**. Heating **1b** with 1 equiv. of [Hg(C≡CPh)$_2$] in refluxing toluene leads as in the case of **1a** to the deposition of elemental mercury, however the only organometallic complex isolated is unreacted **1b**. Indeed if **1b** is treated under similar conditions with a tenfold excess of [Hg(C≡CPh)$_2$] the only isolated species (after 2 min) are **1b**, elemental mercury and diphenylbutadiyne. Thus the complex **1b** catalyses the extrusion of mercury from [Hg(C≡CPh)$_2$]. Heating [Hg(C≡CPh)$_2$] alone in refluxing toluene fails to produce mercury deposition thereby confirming the complicity of **1b** in the reaction. The mechanism for this reaction would appear to reflect, at least initially, that for the formation of **1a**. In the osmium case, however the complex [Os{C(=CHPh)C≡CPh}Cl(CO)(PPh$_3$)$_2$] **2d** is unstable under the reaction conditions, proceeding *via* β-Os–H elimination to provide 'OsHCl(CO)(PPh$_3$)$_2$' for re-entry into the catalytic manifold (Scheme 1). These observations led us to investigate the reaction of [Hg(C≡CPh)$_2$] with 5 mol% of **2a** which led after 1–2 min to the formation of PhC≡CC≡CPh and recovery of **2a**. Furthermore similar treatment of **2a** with [Hg(C≡CC$_6$H$_4$Me)$_2$] provided MeC$_6$H$_4$C≡CC≡CC$_6$H$_4$Me and **2b**, thereby verifying the proposed mechanism.

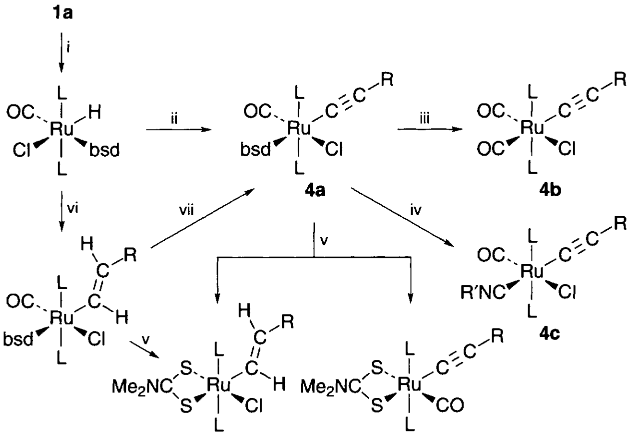


Scheme 1 Catalytic demercuration of bis(alkynyl)mercurials by **1b** (L = PPh$_3$, R = Ph, C$_6$H$_4$Me, Bu^n)

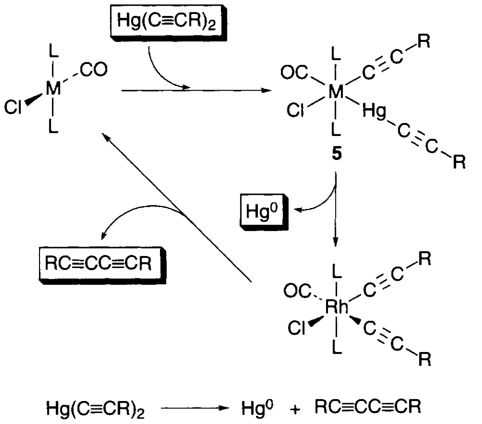
In the initial preparation of **1a**, the facile reaction of the putative intermediate complex [Ru(C≡CR)Cl(CO)(PPh$_3$)$_n$] (*n* = 2, 3, ?) with terminal alkynes is presumed to be due to the lability of one of the bulky triphenylphosphine ligands. Accordingly, the reactions of the complex [RuClH-(CO)(bsd)(PPh$_3$)$_2$] **3** (bsd = 2,1,3-benzoselenadiazole)[5] with Hg(C≡CR)$_2$ (R = Bu^n, C$_6$H$_4$Me-4, Ph) were investigated, assuming that bsd would compete more effectively with alkyne than PPh$_3$. The complexes [Ru(C≡CR)Cl(CO)(bsd)(PPh$_3$)$_2$] **4a** were obtained in good yield under surprisingly mild conditions (CH$_2$Cl$_2$, 25 °C, 30 min) accompanied by the formation of 1 equiv. of free alkyne and elemental mercury. Similar results are obtained with the hydride complexes [RuClH(CO)(PPh$_3$)$_2$L′] (L′ = pyridine, dimethylpyrazole) however the products are colourless or pale yellow. The bsd ligand is apparently sufficiently strongly bound to prevent reaction with liberated RC≡CH, but labile enough to be replaced by sterically modest π-acidic ligands 'L' (CO, CNR) to provide stable octahedral acetylide complexes [Ru(C≡CR)Cl(CO)(PPh$_3$)$_2$L] (L = CO **4b**;‡ CNC$_6$H$_3$Me$_2$-2,6 **4c**), one example of which (**4b**, R = C$_6$H$_4$Me-4) has been crystallographically characterised.§ The dicarbonyl derivatives could also be prepared by the reaction of [Ru(CH=CHPh)Cl(bsd)(CO)(PPh$_3$)$_2$] with an excess of RC≡CH in refluxing ethanol, followed by addition of CO (Scheme 2). Reaction of [Ru(C≡CC$_6$H$_4$Me-4)Cl(bsd)(CO)(PPh$_3$)$_2$] with Na(S$_2$CNMe$_2$) in CH$_2$Cl$_2$–EtOH leads to the formation of [Ru(C≡CC$_6$H$_4$Me-4)(S$_2$CNMe$_2$)(CO)(PPh$_3$)$_2$] along with a small amount of a second compound identified as [Ru(CH=CHC$_6$H$_4$Me-4)(S$_2$CNMe$_2$)(CO)(PPh$_3$)$_2$] which could be prepared independently by the reaction of Na(S$_2$CNMe$_2$) with [Ru(CH=CHC$_6$H$_4$Me-4)Cl(bsd)(CO)(PPh$_3$)$_2$].[5]

It is perhaps surprising that **4a** fails to react cleanly with electrophiles at the carbon β to ruthenium (to form vinylidenes) in contrast to the copious precedent for acetylides of divalent ruthenium.[4] Rather, reaction with HCl leads to cleavage of the acetylide and formation of [RuCl$_2$(CO)$_2$(PPh$_3$)$_2$] suggesting protonation at the ruthenium–carbon bond or ruthenium itself followed by reductive elimination. We note that all successful acetylide to vinylidene conversions on divalent ruthenium have so far involved complexes with donor ligands (rather than π-acids) coordinated *trans* to the acetylide.

Collman and Kang have reported the oxidative addition of bis(phenylethynyl)mercury to Vaska's complex to provide the complex $[Ir(C{\equiv}CPh)(HgC{\equiv}CPh)Cl(CO)(PPh_3)_2]$ **5a**.[6] We considered that such a strategy might provide access to bis(alkynyl) complexes of rhodium following thermal extrusion of mercury from the presumably more labile Rh–Hg–C linkage, given that we have observed **5a** to be both thermally and photochemically labile. The reaction of $[RhCl(CO)(PPh_3)_2]$ with $[Hg(C{\equiv}CPh)_2]$ does not however *ultimately* provide $[Rh(C{\equiv}CPh)(HgC{\equiv}CPh)Cl(CO)(PPh_3)_2]$ **5b**. Rather, following deposition of elemental mercury, only unreacted $[RhCl(CO)(PPh_3)_2]$ is obtained in addition to diphenylbutadiyne. Furthermore we find that the complex $[Rh(CO)(PPh_3)_2\{H_2B(bta)_2\}]$ (bta = benzotriazolyl)[7] also behaves in a similar manner. The mechanism for this catalytic demercuration is therefore presumably as shown in Scheme 3 and is clearly distinct from that in Scheme 1.



Scheme 2 *Reagents and conditions*: i, bsd, thf, heat; ii, Hg $(C{\equiv}CR)_2$, CH_2Cl_2, 25 °C; iii, CO, CH_2Cl_2, 25 °C; iv, CNR′, CH_2Cl_2, 25 °C; v, $NaS_2CNMe_2{\cdot}2H_2O$, CH_2Cl_2–EtOH; vi, HC≡CR, thf, heat; vii, HC≡CR, EtOH, heat (L = PPh_3, R = C_6H_4Me; R′ = $C_6H_3Me_2$)



Scheme 3 Catalytic demercuration of bis(alkynyl)mercurials by $[RhCl(CO)(PPh_3)_2]$ (L = PPh_3, R = Ph, C_6H_4Me, Bu^n)

To conclude, two catalytic cycles for the demercuration of bis(alkynyl)mercurials have been demonstrated. Furthermore novel hydride/acetylide metathesis has been shown to be effected under very mild conditions by transalkynylation. The convenience of preparation of alkynyl mercurials[2] makes these routes to both butadiynes and σ-acetylides attractive.

We gratefully acknowledge the EPSRC (UK) for financial support and Johnson Matthey Chemicals Ltd for a generous loan of platinum group metal salts.

Footnotes

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‡ *Selected data for* **4b**: Yield (1.0 mmol scale) 0.77 g (93%). IR (Nujol): 1986, 2048 (ν_{CO}), 2111 ($\nu_{C\equiv C}$). NMR ($CDCl_3$, 25 °C): ^1H δ 2.27 (s, 3 H, Me), 6.74, 6.90 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 7.9 Hz]; $^{13}C\{^1H\}$ δ 194.6 [t, RuCO, *J*(PC) 11.6 Hz], 192.0 [t, RuCO, *J*(PC) 8.0 Hz], 115.5 (s, Ru$C{\equiv}$*C*), 106.8 [t, Ru*C*≡C, *J*(PC) 19.7 Hz], 21.3 [CH_3]; $^{31}P\{^1H\}$ δ 23.1. FAB MS *m/z* 832 $[M]^+$, 804 $[M - CO]^+$, 797 $[M - Cl]^+$, 717 $[M - CCR]^+$, 689 $[M - CCR - CO]^+$, $[RuCO(PPh_3)_2]^+$, 625 $[Ru(PPh_3)_2]^+$, 363 $[RuPPh_3]^+$.

§ *Crystal data for* **4b**: $C_{47}H_{37}ClO_2P_2Ru{\cdot}0.75CHCl_3$, M = 921.8, monoclinic, space group $P2_1/n$, a = 10.216(2), b = 37.395(8), c = 23.007(3) Å, β = 102.29(1)°, U = 8588(3) Å^3, Z = 8 (two crystallographically independent molecules in the asymmetric unit), D_c = 1.43 g cm^{-3}, μ(Mo-Kα) = 0.68 mm^{-1}, $F(000)$ = 3756. 15 118 Independent reflections (Mo-Kα radiation; graphite monochromator, ω-scans). R_1 = 0.068, wR_2 = 0.127 for 8663 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta < 50°$] and 879 parameters. Whilst the analysis unambiguously defined the identity and stereochemistry of the complex, minor structural anomalies in the bond lengths precluded detailed discussion. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/25.

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Received, 30th November 1995; Com. 5/07820B