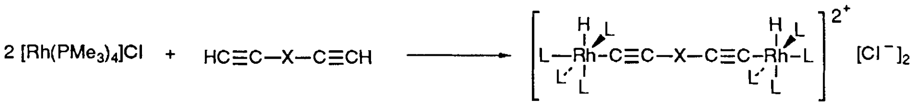
Synthesis of Mononuclear, Dinuclear and Oligomeric Rigid-rod Acetylide Complexes of Rhodium, and the Molecular Structure of $[Rh(PMe_3)_4(C{\equiv}C\text{-}p\text{-}C_6H_4\text{-}C{\equiv}C)Rh(PMe_3)_4]$

Helen B. Fyfe, Michael Mlekuz, David Zargarian, Nicholas J. Taylor and Todd B. Marder*

Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Reaction of two equivalents of $[Rh(PMe_3)_4]Cl$ with $HC{\equiv}C\text{-}X\text{-}C{\equiv}CH$ (X = none, $p\text{-}C_6H_4$, $p\text{-}C_6F_4$, $p\text{-}C_6H_4\text{-}C_6H_4\text{-}p$) yields the dinuclear acetylide bridged dications *cis-cis*-$[Rh(PMe_3)_4(H)(C{\equiv}C\text{-}X\text{-}C{\equiv}C)Rh(PMe_3)_4(H)]^{2+}[Cl^-]_2$, whereas reaction of $[Rh(PMe_3)_4(Me)]$ with $HC{\equiv}C\text{-}X\text{-}C{\equiv}CH$ (X = $p\text{-}C_6H_4$, $p\text{-}C_6H_4\text{-}C_6H_4\text{-}p$) yields neutral mononuclear, dinuclear or oligomeric rigid-rod complex *mer-trans*-$[Rh(PMe_3)_3(H)(C{\equiv}C\text{-}X\text{-}C{\equiv}CH)_2]$, $[Rh(PMe_3)_4(C{\equiv}C\text{-}X\text{-}C{\equiv}C)Rh(PMe_3)_4]$ or *mer-trans*-$[\text{-}Rh(PMe_3)_3(H)\text{-}C{\equiv}C\text{-}X\text{-}C{\equiv}C\text{-}]_n$, depending upon the stoichiometry employed (1 : 2, 2 : 1, or 1 : 1 respectively); the crystal and molecular structure of the dinuclear Rh^I complex $[Rh(PMe_3)_4(C{\equiv}C\text{-}C_6H_4\text{-}C{\equiv}C)Rh(PMe_3)_4]$ has been determined by X-ray diffraction, and soluble rigid-rod oligomers have been isolated from reactions employing the $PBu^n{}_3$ ligand.

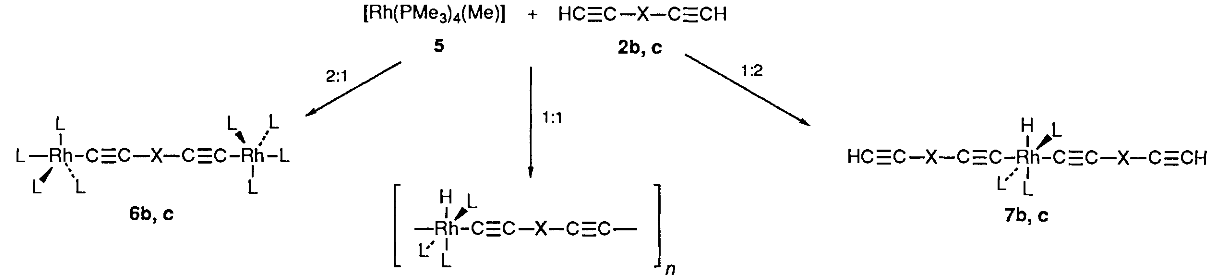
Transition metal acetylide complexes represent a class of linear conjugated molecules that can exhibit both second- and third-order optical nonlinearities. We recently reported[1] the synthesis and second-order nonlinear optical behaviour of a series of unsymmetrically substituted *trans*-bis(acetylide) complexes of platinum of the general form *trans*-$[Pt(PMe_2Ph)_2(C{\equiv}C\text{-}D)(C{\equiv}C\text{-}A)]$, where D and A represent π-donor and π-acceptor groups respectively. Large third-order optical nonlinearities ($\chi^{(3)}$) result[2] from highly conjugated organic π-systems such as polyacetylenes and polydiacetylenes. Rigid-rod poly-ynes of the form *trans*-$[Pt(PBu^n{}_3)_2(\text{-}C{\equiv}C\text{-}X\text{-}C{\equiv}C\text{-})_n$, originally prepared[3] by the Hagihara group, have been shown to exhibit both liquid crystalline behaviour[4] and large third-order optical nonlinearities.[5] In an effort to examine the role of the transition metal and the acetylide linker groups on the magnitude of $\chi^{(3)}$, we have developed a new high-yield method for preparing dinuclear and oligomeric rhodium complexes linked by a



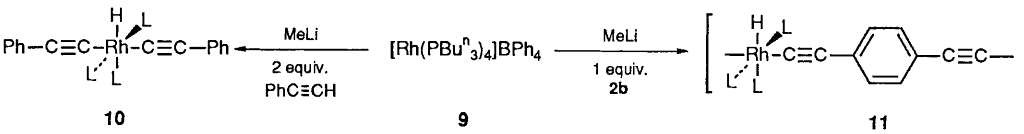
1 2 3

a; X = none
b; X = $p\text{-}C_6H_4$
c; X = $p\text{-}C_6H_4\text{-}C_6H_4\text{-}p$
d; X = $p\text{-}C_6F_4$

Scheme 1 L = PMe_3



Scheme 2 L = PMe_3



Scheme 3 L = PBu^n_3

conjugated acetylide ligand. Our synthetic approach yields the desired species directly from the appropriate terminal dialkynes, with methane and PR_3 being the only byproducts.

We previously reported[6] that terminal alkynes RC≡CH react cleanly with $[Rh(PMe_3)_4]Cl$ **1** *via* C–H oxidative addition giving the cationic complexes *cis*-$[Rh(PMe_3)_4(H)(C{\equiv}CR)]Cl$ in excellent yields. We find that reaction of two equivalents of **1** with HC≡C–C≡CH **2a** or HC≡C–X–C≡CH (X = *p*-C_6H_4, **2b**; *p*-C_6H_4–C_6H_4-*p*, **2c**; *p*-C_6F_4, **2d**) in tetrahydrofuran (THF) suspension yields the dinuclear dications[†] *cis-cis*-$[Rh(PMe_3)_4(H)(C{\equiv}C{-}X{-}C{\equiv}C)Rh(PMe_3)_4(H)]^{2+}[Cl^-]_2$ **3a–d** directly, as precipitates (Scheme 1). In some cases, small amounts of the THF-soluble neutral *cis*-hydrido-acetylides *mer*-$[Rh(PMe_3)_3(Cl)(H)(C{\equiv}C{-}X{-}C{\equiv}CH)]$ **4** remain in solution. Deprotonation of **3a–d** with aqueous KOH would yield the neutral dinuclear Rh^I complexes $[Rh(PMe_3)_4(C{\equiv}C{-}X{-}C{\equiv}C)Rh(PMe_3)_4]$ **6**, as reported previously[7] for mononuclear analogues. The electron-rich Rh^I acetylides $[Rh(PMe_3)_4(C{\equiv}CR)]$ react[8] with terminal alkynes giving *mer-trans*-$[Rh(PMe_3)_3(H)(C{\equiv}CR)_2]$. Extension of this route to **6** would give rise to oligomers if diynes such as **2a–d** were employed. However, this methodology requires several steps, and a more direct synthesis would be desirable.

Reaction of two equivalents of $[Rh(PMe_3)_4(Me)]$ **5** with one equivalent of **2b,c** in THF yields **6**[†] directly with loss of CH_4 (Scheme 2). The molecular structure[‡] of **6b** is illustrated in Fig. 1. The structure of *trans*-$[Pt(PEt_3)_2(NCS)(C{\equiv}C$-*p*-$C_6H_4$–$C{\equiv}C)Pt(PEt_3)_2(NCS)]$ has been reported.[9] The trigonal bipyramidal geometry and the bond distances and angles in **6b** are similar to those[7] in $[Rh(PMe_3)_4(C{\equiv}CPh)]$.

Reaction of **5** with **2b,c** in the *reverse* stoichiometry (*i.e.* 1:2) yields the mononuclear Rh^{III} complexes *mer-trans*-$[Rh(PMe_3)_3(H)(C{\equiv}C{-}X{-}C{\equiv}CH)_2]$ **7b,c**.[†] Complexes **7b,c** are analogues of *mer-trans*-$[Rh(PMe_3)_3(H)(C{\equiv}CPh)_2]$, which has been structurally characterized.[8] Thus, both the Rh centre and the diynes are effectively bifunctional monomers, and reaction of **5** with **2b,c** in 1:1 stoichiometry should yield linear rigid-rod polymers. Indeed, the poly-yne polymers **8b,c** are isolated as white–beige powders in quantitative yields. Unlike the mono- and di-nuclear species **6b,c** and **7b,c**, oligomers **8b,c** are insoluble in common organic solvents. However, they were characterized by IR spectra of Nujol mulls[†] that exhibit ν_{Rh-H} and $\nu_{C\equiv C}$ stretches identical to those of **7b,c**. Preliminary solid-state ^{13}C and ^{31}P NMR spectra of **8b** are also consistent with the proposed structure. In addition, solubility properties and $\nu_{C\equiv C}$ for **8c** are virtually identical to those for the analogous oligomer *mer-trans*-$[Rh(PMe_3)_3(SnMe_3)(C{\equiv}C$–$C_6H_4$–$C_6H_4$–$C{\equiv}C)]_n$ prepared by the Lewis group.[10]

In order to obtain soluble, processible analogues of **8b,c** we have carried out a preliminary study (Scheme 3) employing

---

[†] *Selected spectroscopic data* (*J* values in Hz) for **3a**: ^1H NMR (CD_3CN) δ 1.61 (virtual t, $^2J_{P\text{-}H}$ 3.4), 1.49 (d, $^2J_{P\text{-}H}$ 8.5), 1.42 (d, $^2J_{P\text{-}H}$ 8.1 and −10.51 (dquint, $^2J_{Ptrans\text{-}H}$ 179, $J_{Rh\text{-}H} = {}^2J_{Pcis\text{-}H} = 17$); $^{31}P\{^1H\}$ NMR (CD_3CN) δ −7.1 (dt, $J_{Rh\text{-}P}$ 87, $^2J_{P\text{-}P}$ 27), −12.9 (dq, $J_{Rh\text{-}P}$ 90, $^2J_{P\text{-}P}$ 27) and −24.4 (dq, $J_{Rh\text{-}P}$ 75, $^2J_{P\text{-}P}$ 27). **3b**: IR (Nujol) 2108 ($\nu_{C\equiv C}$) and 1975 cm^{-1} (ν_{Rh-H}); ^1H NMR (CD_3CN) δ 7.09 (s) and −10.39 (dquint, $^2J_{Ptrans\text{-}H}$ 179, $J_{Rh\text{-}H} = {}^2J_{Pcis\text{-}H} = 18$); $^{31}P\{^1H\}$ NMR (CD_3CN) δ −6.5 (dt, $J_{Rh\text{-}P}$ 87, $^2J_{P\text{-}P}$ 28), −13.0 (dq, $J_{Rh\text{-}P}$ 90, $^2J_{P\text{-}P}$ 28) and −24.1 (dq, $J_{Rh\text{-}P}$ 76, $^2J_{P\text{-}P}$ 28). **3c**: IR (Nujol) 2107 and 1984 cm^{-1}; ^1H NMR (CD_3CN) δ 7.39 (AB q) and −10.36 (dquint, $^2J_{Ptrans\text{-}H}$ 179, $J_{Rh\text{-}H} = {}^2J_{Pcis\text{-}H} = 17$). **3d**: IR (Nujol) 2107 and 1964 cm^{-1}; ^1H NMR (CD_3CN) δ −10.28 (dquint, $^2J_{Ptrans\text{-}H}$ 175, $J_{Rh\text{-}H} = {}^2J_{Pcis\text{-}H} = 18$).

6b: IR (Nujol) 2080 cm^{-1}; ^1H NMR (C_6D_6) δ 7.44 (s, 4H), 1.31 (d, $^2J_{P\text{-}H}$ 5.3, 72 H); $^{31}P\{^1H\}$ NMR (THF, 193 K) δ 2.6 (br s, $1PMe_3$) and −24.9 (br d, $J_{Rh\text{-}P}$ 144, $3PMe_3$). **6c**: IR (Nujol) 2075 cm^{-1}; ^1H NMR (C_6D_6) δ 7.53 (AB q).

7b: IR(Nujol) 3296 ($\nu_{\equiv C-H}$), 2084 ($\nu_{C\equiv C}$) and 1941 cm^{-1} (ν_{Rh-H}); ^1H NMR (C_6D_6) δ 7.35 (AB q, 8H), 2.81 (s, 2H), 1.36 (virtual t, J_{P-H} 3.3, 18H), 1.12 (d, $^2J_{P\text{-}H}$ 7.4, 9H) and −9.18 (dq, $^2J_{Ptrans\text{-}H}$ 189, $J_{Rh\text{-}H} = {}^2J_{Pcis\text{-}H} = 18$, 1H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −7.6 (dd, $J_{Rh\text{-}P}$ 93, $^2J_{P\text{-}P}$ 26) and −24.6 (dt, $J_{Rh\text{-}P}$ 76, $^2J_{P\text{-}P}$ 26). **7c**: IR (Nujol) 3274, 2085 and 1942 cm^{-1}; $^{31}P\{^1H\}$ NMR (C_6D_6) δ −6.9 (dd, $J_{Rh\text{-}P}$ 93, $^2J_{P\text{-}P}$ 25 Hz) and −24.4 (dt, $J_{Rh\text{-}P}$ 82, $^2J_{P\text{-}P}$ 25).

8b: IR (Nujol) 3296 vw, 2084 and 1941 cm^{-1}. **8c**: IR (Nujol) 3274 vw, 2085 and 1942 cm^{-1}.

10: IR (neat) 2085 cm^{-1} ($\nu_{Rh\text{-}H}$ not observed); ^1H NMR (C_6D_6) δ −10.18 (dq, $^2J_{Ptrans\text{-}H}$ 174, $J_{Rh\text{-}H} = {}^2J_{Pcis\text{-}H} = 14$); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 14.2 (dd, $J_{Rh\text{-}P}$ 94, $^2J_{P\text{-}P}$ 20) and −8.1 (dt, $J_{Rh\text{-}P}$ 80, $^2J_{P\text{-}P}$ 20); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 112.41 (dq, J_{Rh-C} 34, $^2J_{P\text{-}C}$ 17, Rh–*C*≡) and 109.68 (d, $^2J_{Rh\text{-}C}$ 7, Rh–C≡*C*).

11: IR (neat film) 2080 cm^{-1} ($\nu_{Rh\text{-}H}$ not observed); ^1H NMR ($[^2H_8]THF$) δ −10.50 (dq, $^2J_{Ptrans\text{-}H}$ 172, $J_{Rh\text{-}H} = {}^2J_{Pcis\text{-}H} = 15$); $^{31}P\{^1H\}$ NMR ($[^2H_8]THF$) δ 17.5 (dd, $J_{Rh\text{-}P}$ 95, $^2J_{P\text{-}P}$ 21) and −4.9 (dt, $J_{Rh\text{-}P}$ 77, $^2J_{P\text{-}P}$ 21); ^{13}C (JMODXH, $[^2H_8]THF$) δ 135.05 (s, C–H Ar).

[‡] *Crystal data for* **6b**: $C_{34}H_{76}P_8Rh_2$, $M = 938.5$, monoclinic, space group $P2_1/n$, $a = 9786(2)$, $b = 16.396(4)$, $c = 15.776(5)$ Å, $\beta = 96.87(2)°$, $U = 2513.1(10)$ Å^3, $Z = 2$, $D_c = 1.240$ g cm^{-3}, $F(000) = 980$, $\lambda = 0.71073$ Å, $T = 200 \pm 1$ K, μ(Mo-Kα) = 9.17 cm^{-1}. Data were collected from a yellow needle of dimensions 0.42 × 0.29 × 0.26 mm on a Siemens R3M/v diffractometer by the ω scan method ($4.0° \leqslant 2\theta \leqslant 55.0°$). The structure was solved by Patterson and Fourier techniques using 2974 observed data [$F > 6.0\sigma(F)$] from 5822 independent measurements and refined by full-matrix least-squares analysis to $R = 0.0307$ and $R_w = 0.0312$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centres. See Notice to Authors, Issue No. 1.

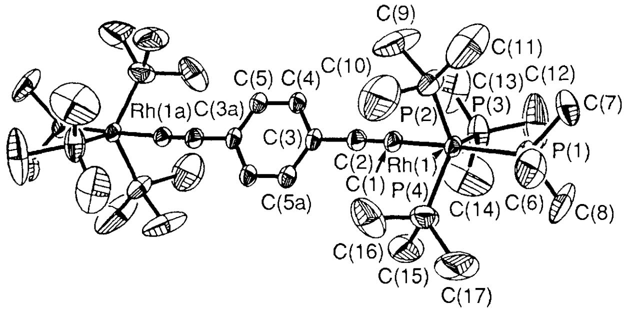


Fig. 1 Molecular structure of **6b**. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles(°): Rh(1)–P(1) 2.281(2), Rh(1)–P(2) 2.304(2), Rh(1)–P(3) 2.314(2), Rh(1)–P(4) 2.290(2), Rh(1)–C(1) 2.014(4), C(1)–C(2) 1.209(6), C(2)–C(3) 1.438(6), C(3)–C(4) 1.395(6), C(4)–C(5) 1.378(6), C(3)–C(5a) 1.397(6), P(1)–Rh(1)–C(1) 177.4(1), P(2)–Rh(1)–C(1) 84.9(1), P(3)–Rh(1)–C(1) 84.3(1), P(4)–Rh(1)–C(1) 80.3(1), Rh(1)–C(1)–C(2) 177.3(4), C(1)–C(2)–C(3) 177.7(5).

PBu^n_3 in place of PMe_3. As a test case, treatment of $[Rh(PBu^n_3)_4]BPh_4$ **9**[11] with MeLi gives a Rh–Me complex, which reacts cleanly with an excess of PhC≡CH, yielding *mer-trans*-$[Rh(PBu^n_3)_3(H)(C{\equiv}CPh)_2]$ **10**[†] as an oil. The analogous reaction using one equivalent of **2b** yields a polymer which is soluble in THF but not in benzene, and which forms free-standing films upon evaporation of solvent. The major component is the desired rigid-rod *mer-trans*-$[Rh(PBu^n_3)_3(H)(\text{–}C{\equiv}C\text{–}C_6H_4\text{–}C{\equiv}C\text{)–}]_n$ **11**, which has similar spectroscopic properties[†] to those of **10**.

We have demonstrated a new route to dinuclear and oligomeric rigid-rod metal acetylides *via* C–H activation. The only byproducts of the polymerisation reactions are CH_4 and PR_3. Efforts are underway to utilise the complex $[Rh(PBu^n_3)_3(Me)]$ and *trans*-$[M(R_2PCH_2CH_2PR_2)_2(Me)_2]$ (M = Fe, Ru) as polymer precursors, from which methane would be the *only* byproduct.[12] Further studies of the physical and optical properties of the new soluble polymers are in progress.

We thank the Research Corporation, the Natural Sciences and Engineering Research Council of Canada, and the Ontario Centre for Materials Research for support, the DuPont Company for a gift of materials and supplies, Johnson Matthey Chemicals Ltd for a loan of precious metals, Dr L. H. Randall and Professor C. Fyfe for the solid-state NMR spectra, and Professor The Lord Lewis for communication of results prior to publication.

Received, 23rd October 1990; Com. 0/04776G

References

1 T. B. Marder, G. Lesley, Z. Yuan, H. B. Fyfe, P. Chow, G. Stringer, I. R. Jobe, N. J. Taylor, I. D. Williams and S. K. Kurtz, in *Materials for Nonlinear Optics: Chemical Perspectives*, ed. G. D. Stucky, S. R. Marder and J. Sohn, *ACS Symp. Ser.* 455, American Chemical Society, Washington, DC, 1991, in the press.

2 See for example: D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 690; *Nonlinear Optical Properties of Organic Molecules and Crystals*, vols. 1 and 2, ed. D. S. Chemla and J. Zyss, Academic Press, Orlando, FL, 1987; *Organic Materials for Non-Linear Optics*, ed. R. A. Hahn and D. Bloor, *Spec. Publ. No. 69*, The Royal Society of Chemistry, London, 1989.

3 See, for example: N. Hagihara, K. Sonogashira and S. Takahashi, *Adv. Polym. Sci.*, 1981, **41**, 149; S Takahashi, H. Morimoto, E. Murata, S. Kataoka, K. Sonogashira and N. Hagihara, *J. Polym. Sci., Polym. Chem. Ed.*, 1982, **20**, 565.

4 S. Takahashi, Y. Takai, H. Morimoto and K. Sonogashira, *J. Chem. Soc., Chem. Commun.*, 1984, 3, and references therein.

5 C. C. Frazier, S. Guha, W. P. Chen, M. P. Cockerham, P. L. Porter, E. A. Chauchard and C. H. Lee, *Polymer*, 1987, **28**, 553; C. C. Frazier, E. A. Chauchard, M. P. Cockerham and P. L. Porter, *Mat. Res. Soc. Symp. Proc.*, 1988, **109**, 323; S. Guha, C. C. Frazier, K. Kang and S. E. Finberg, *Optics Lett.*, 1989, **14**, 952; C. C. Frazier, S. Guha and W. Chen, P.C.T. Int. Appl. WO 89 01,182, Feb. 1989; U.S. Appl. 81,785, Aug. 1987 (*Chem. Abstr.* 1989, **111**, 10 5446 p).

6 T. B. Marder, D. Zargarian, J. C. Calabrese, T. Herskovitz and D. Milstein, *J. Chem. Soc., Chem. Commun.*, 1987, 1484.

7 D. Zargarian, P. Chow, N. J. Taylor and T. B. Marder, *J. Chem. Soc., Chem. Commun.*, 1989, 540.

8 P. Chow, D. Zargarian, N. J. Taylor and T. B. Marder, *J. Chem. Soc., Chem. Commun.*, 1989, 1545.

9 U. Behrens, K. Hoffmann, J. Kopf and J. Moritz, *J. Organomet. Chem.*, 1976, **117**, 91.

10 S. J. Davies, B. F. G. Johnson, M. S. Khan and J. Lewis, preceding communication.

11 L. Haines, *Inorg. Chem.*, 1970, **9**, 1517.

12 For related iron monomers, see: L. D. Field, A. V. George, T. W. Hambley, E. Y. Malouf and D. J. Young, *J. Chem. Soc., Chem. Commun.*, 1990, 931.