ELSEVIER

Journal of Organometallic Chemistry 578 (1999) 264–267

Journal of Organometallic Chemistry

Preliminary communication

Unprecedented coupling of vinylidene and allenylidene ligands with dithiocarbamates: X-ray structure of $[Ru\{C(=C=CPh_2)SC(NMe_2)S\}(S_2CNMe_2)(CO)(PPh_3)]$

Beatrice Buriez, Darren J. Cook, Karsten J. Harlow, Anthony F. Hill *, Thomas Welton [1], Andrew J.P. White, David J. Williams, James D.E.T. Wilton-Ely

Centre for Chemical Synthesis, Department of Chemistry, Imperial College of Science Technology and Medicine, South Kensington, London SW7 2AY, UK

Received 27 August 1998

Abstract

The reaction of $[RuCl(PPh_3)_2\{HB(pz)_3\}]$ (pz = pyrazol-1-yl) with 4-ethynyl toluene provides $[RuCl(=C=CHC_6H_4Me\text{-}4)(PPh_3)\{HB(pz)_3\}]$ (**1a**) which reacts with $[Et_2NH_2][S_2CNEt_2]$ to give the metallacyclic alkenyl complex $[Ru\{C(=CHC_6H_4Me\text{-}4)SC(NEt_2)S\}(PPh_3)\{HB(pz)_3\}]$ (**2**). The reaction of $[RuCl(PPh_3)_2\{HB(pz)_3\}]$ with diphenylpropynol and $Ag[PF_6]$ however provides $[Ru(=C=C=CPh_2)(PPh_3)_2\{HB(pz)_3\}]PF_6$ (**3**) or in the absence of silver salts, the neutral complex $[RuCl(=C=C=CPh_2)(PPh_3)\{HB(pz)_3\}]$ (**4**). Both (**3**) and (**4**) react with $Na[S_2CNMe_2]$ to give the metallacyclic allenyl complex $[Ru\{C(=C=CPh_2)SC(NMe_2)S\}(PPh_3)\{HB(pz)_3\}]$ (**5**). Treatment of $[RuHCl(CO)(PPh_3)_3]$ with diphenylpropynol and $Na[S_2CNMe_2]$ provides $[Ru(CH=CHCPh_2OH)(S_2CNMe_2)(CO)(PPh_3)_2]$ which reacts with excess diphenylpropynol to give the alkynyl complex $[Ru(C\equiv CCPh_2OH)(S_2CNMe_2)(CO)(PPh_3)_2]$. Protonation of this complex with HBF_4 provides the allenylidene complex $[Ru(=C=C=CPh_2)(S_2CNMe_2)(CO)(PPh_3)_2]BF_4$ (**6**) which reacts with $Na[S_2CNMe_2]$ to give a kinetic isomer (**7k**) and ultimately a structurally characterised thermodynamic isomer of the metallacyclic allenyl complex $[Ru\{C(=C=CPh_2)SC(NMe_2)S\}(S_2CNMe_2)(CO)(PPh_3)]$ (**7t**). © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Vinylidene; Allenylidene; Dithiocarbamate; Metallacycle; Ligand-coupling; Ruthenium

---

1. Introduction

The incorporation of metal centres into electronically conjugated carbon-rich systems, offers enormous promise for electro-optical applications [1]. The metal centres investigated to date have typically employed sets of traditionally ‘innocent’ co-ligands, e.g. phosphines, carbonyls, arenes and cyclopentadienyls. Dithiocarbamates present themselves as potentially useful co-ligands for such applications for three reasons: (i) their high and tunable $\sigma+\pi$ basicity towards the metal centre, a feature which should facilitate MLCT photochemical events for unsaturated organometallic π-acid co-ligands; (ii) the characteristically high stability of their complexes; and (iii) a long tradition of innocent behaviour as spectator co-ligands. It is this last property which we call into question in the present work. We have recently observed that metallacyclic dithiocarbamatoalkyls can result from the coupling of alkylidene and dithiocarbamate ligands [2,3]. We were therefore curious as to whether such dithiocarbamate coupling reactions might be extended to other ‘C_1’ π-acid ligands

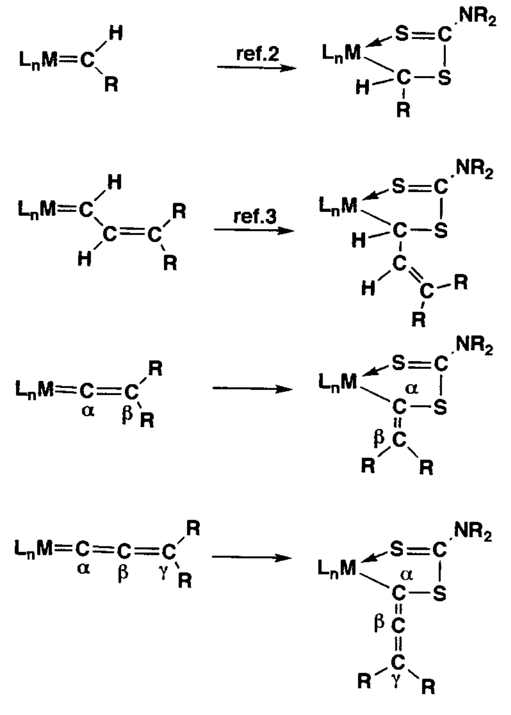
---

* Corresponding author.

E-mail address: a.hill@ic.ac.uk (A.F. Hill)

[1] Also corresponding author.

PII: S0022-328X(98)01130-9



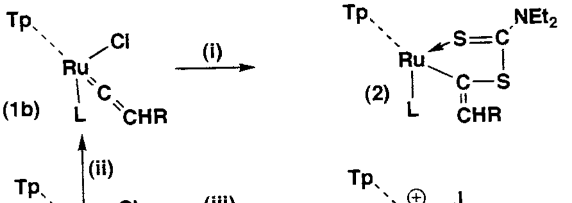
Scheme 1. Dithiocarbamate coupling with unsaturated C_1 π-acid ligands and NMR designations.

which feature more extended unsaturation. We report herein the reactions of dithiocarbamate salts with a range of new vinylidene and allenylidene complexes of ruthenium. These lead in all cases to novel metallacyclic vinyl or allenyl ligands which result from the novel coupling of dithiocarbamate and vinylidene or allenylidene ligands (Scheme 1).

2. Results and discussion

The complex $[RuCl(=C=CHC_6H_4Me)(PPh_3)\{HB(pz)_3\}]$ (pz = pyrazol-1-yl) (**1a**) results from $[RuCl(PPh_3)_2\{HB(pz)_3\}]$ [3] and 4-ethynyl toluene, in a manner analogous to that previously described for $[RuCl(=C=CHPh)(PPh_3)\{HB(pz)_3\}]$ (**1b**) [4]. Treating (**1a**) with $[Et_2NH_2][S_2CNEt_2]$ in tetrahydrofuran provides a yellow complex (40%) (Scheme 2), spectroscopic data for which identify it as the metallacycle $[Ru\{C(=CHC_6H_4Me\text{-}4)SC(NEt_2)S\}(PPh_3)\{HB(pz)_3\}]$ (**2**) resulting from the coupling of vinylidene and dithiocarbamate ligands. [IR: 2464 (BH), 1529w, 1309w, 1265m, 1213m, 1114m, 1043m, 865w, 813 $[\delta(C_6H_4)]$ cm^{-1}. ^{1}H-NMR: δ 0.99, 1.11 [m(br) × 2, 6 H, $CH_2C\underline{H}_3$], 2.36 [s, 3 H, $C_6H_4C\underline{H}_3$], 3.2, 3.4, 3.7, 4.23 [m(br) × 4, 4 H, NCH_2], 5.88–7.78 [29 H, RuC=CH, PC_6H_5 and pz]. $^{13}C\{^1H\}$-NMR: 206.0 [s, CS_2], 173.2 [d, RuC, $J_{PC} = 11.9$ Hz], 144.8, 144.6, 142.1 [C^3(pz)], 138.3 [RuC=$\underline{C}$H], 135.5, 135.3, 135.0 [C^5(pz)], 134.6–127.1 [$PC_6H_5 + C_6H_4$], 105.1, 104.7 [C^4(pz)], 52.5, 47.3 [br, NCH_2], 21.2 [$C_6H_4\underline{C}H_3$], 12.1 [$CH_2\underline{C}H_3$] ppm. $^{31}P\{^1H\}$-NMR: 58.6 ppm. FAB-MS 841[M]$^+$]. We have been unsuccessful in obtaining crystallographic grade crystals of (**2**), however a related and structurally characterised metallacycle is discussed below.

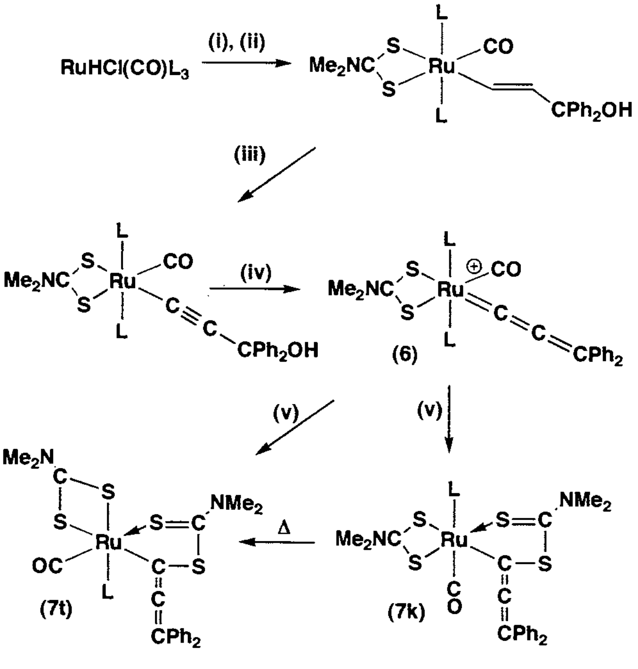
Following Selegue's original synthesis of $[Ru(=C=C=CPh_2)(PMe_3)_2(\eta\text{-}C_5H_5)]PF_6$ [5], numerous allenylidene complexes of ruthenium have followed from his 2-propynol dehydration approach [6]. The reactions of $[RuCl(PPh_3)_2\{HB(pz)_3\}]$ with $HC{\equiv}CCPh_2OH$ were therefore investigated: In the presence of $AgPF_6$, the structurally characterised [7] salt, $[Ru(=C=C=CPh_2)(PPh_3)_2\{HB(pz)_3\}]PF_6$ (**3**) is obtained. However, in its absence the neutral allenylidene complex $[RuCl(=C=C=CPh_2)(PPh_3)\{HB(pz)_3\}]$ (**4**) is obtained (Scheme 2). The formulations of (**3**) and (**4**) follow unambiguously from spectroscopic data [(**3**) IR: 2472m (BH), 2073m, 1938s (Ru=C=C=C, 1943 in CH_2Cl_2), 1483s, 1313m, 1255m, 1220w, 1144w, 1120w, 844 (PF_6) cm^{-1}. ^{1}H-NMR: δ 4.6 [s(vbr) 1 H, BH], 5.59, 5.64 [t × 2, 2 H + 1 H, H^4(pz), $J_{HH} = 2$], 5.68, 6.10 [d × 2, 1 H + 2 H, H^3(pz), $J_{HH} = 2$ Hz], 6.55–7.88 [40 H, C_6H_5 and H^5(pz)] ppm. $^{13}C\{^1H\}$-NMR: 316.6 [t, Ru = C_α, $J_{P_2C} = 17.8$ Hz], 208.9 [s, C_β], 160.9 [s, C_γ], 146.5, 145.0 [C^3(pz)], 144.2 [$C^1(CC_6H_5)$], 137.0, 136.7 [C^5(pz)], 133.8–128.4 [$CC_6H_5 + PC_6H_5$], 106.7, 105.8 [C^4(pz)] ppm. $^{31}P\{^1H\}$-NMR: 36.5 ppm. FAB-MS 1029 [M]$^+$. (**4**) IR: 2476w (BH), 1914s (Ru=C=C=C, 1920 in CH_2Cl_2), 1309m, 1213m, 1116m, 1047s cm^{-1}. ^{1}H-NMR: δ 5.61–7.74 [pz and C_6H_5] ppm. $^{13}C\{^1H\}$-NMR: 313.6 [d, C_α, $J_{PC} = 22.7$ Hz], 230.6 [C_β], 146.4–126.1 [C_6H_5, and $C^{3,5}$(pz)], 106.0, 105.4 [C^4(pz)] ppm. $^{31}P\{^1H\}$-NMR: 38.0 ppm. FAB-MS 802 [M]$^+$].



Scheme 2. Reagents, conditions and yields. L = PPh_3, Tp = $HB(pz)_3$; R = C_6H_4Me-4. (i) $[Et_2NH_2][S_2CNEt_2]$, thf, 25°C, 1.5 h 40%; (ii) $HC{\equiv}CR$, thf, 25°C, 36 h, 75%; (iii) $HC{\equiv}CCPh_2OH$, $Ag[PF_6]$, CH_2Cl_2, 3.5 h, 89%; (iv) $HC{\equiv}CCPh_2OH$, thf, Δ, 4 h, 66%; (v) $Na[S_2CNMe_2]$, thf, Δ, 2 h, 75% from (**4**).

Both (**3**) and (**4**) react with $Na[S_2CNMe_2]$ to provide the same metallacyclic allenyl complex $[Ru\{C(=C=CPh_2)SC(NMe_2)S\}(PPh_3)\{HB(pz)_3\}]$ (**5**) [IR: 2458w (BH), 1951w, 1594w, 1490m, 1307m, 1211m, 1114m, 1043m, 979w cm^{-1}. ^{1}H-NMR: 3.26 [s, 6 H, NCH_3], 5.67–7.39 [m, 34 H, C_6H_5 and pz]. $^{13}C\{^1H\}$-NMR: 207.9, 201.2 [CS_2, C_β], 145.8, 145.0, 141.9 [C^3(pz)], 140.8 [C_γ], 135.9, 135.4, 135.0 [C^5(pz)], 134.8–124.6 [C_6H_5], 118.5 [d, C_α, $J_{PC} = 12.9$], 105.7 [d, C^4(pz), $J_{PC} = 6.5$ Hz], 105.1, 104.9 [C^4(pz)], 46.0 [v(br), NCH_3] ppm. $^{31}P\{^1H\}$-NMR: 56.1 ppm. FAB-MS 887 [M]$^+$]. Despite the positive charge on the complex in (**3**), this reacts more slowly than (**4**). Thus either steric factors are important, or both (**4**) and more slowly (**3**) provide $[Ru(=C=C=CPh_2)(PPh_3)\{HB(pz)_3\}]^+$ in solution which then reacts with dithiocarbamate. Attack by dithiocarbamate at either ruthenium or C_α is thus plausible and Esteruelas has provided a precedent for the direct attack of thiols at the α-carbon of an allenylidene complex [6e].

To investigate the possibility of direct nucleophilic attack at the allenylidene α-carbon, the new and otherwise substitution–inert complex $[Ru(S_2CNMe_2)(=C=C=CPh_2)(CO)(PPh_3)_2]PF_6$ (**6**) was prepared by the route shown in Scheme 3. This involves (i) the hydroruthenation of $HC\equiv CCPh_2OH$ by $[RuHCl(CO)(PPh_3)_3]$ to provide $[Ru(CH=CHCPh_2OH)Cl(CO)(PPh_3)_2]$; (ii) attainment of coordinative saturation by chloride/dithiocarbamate metathesis; (iii) alkenyl/alkynyl metathesis via alkyne C–H oxidative addition and alkene reductive elimination; (iv) Proton induced γ-dehydroxylation of the γ-hydroxyalkynyl ligand by HPF_6. Spectroscopic data for (**6**) are generally unremarkable other than to confirm the formulation [IR: 2003s, 1943vs (Ru=C=C=C, 2001, 1951 in CH_2Cl_2), 1585w, 1531w, 1309w, 1288w cm^{-1}. ^{1}H-NMR: δ 2.41, 2.46 [s × 2, 3 H × 2, NCH_3], 7.21–7.84 [40 H, C_6H_5]. $^{13}C\{^1H\}$-NMR: 296.7 [t, C_α, $J_{P2C} = 12.4$], 203.1 [CS_2], 198.1 [t, RuCO, J_{P2C} 12.0 Hz], 188.2 [C_β], 166.8 [C_γ], 141.7 [$C^1(CC_6H_5)$], 134.4–127.9 [C_6H_5], 38.4, 38.0 [NCH_3] ppm. $^{31}P\{^1H\}$-NMR: 36.8 ppm. FAB-MS 964 [M]$^+$].



Scheme 3. Reagents, conditions and yields. L = PPh_3 (i) $HC\equiv CCPh_2OH$, Et_2O, 25°C, 12 h, 97%; (ii) $Na[S_2CNMe_2]$, CH_2Cl_2/EtOH, 25°C, 1.5 h, 86%; (iii) $HC\equiv CCPh_2OH$, EtOH, Δ; 72 h, 78%; (iv) $HPF_6 \cdot Et_2O$, 25°C, 15 m, 80%; (v) $Na[S_2CNMe_2]$, $CHCl_3$, Δ, 12 h, 86%.

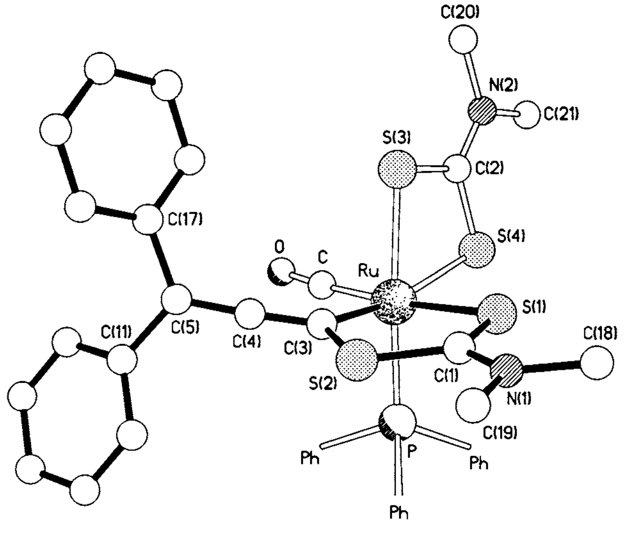


Fig. 1. Molecular structure of (**7t**). Hydrogen atoms and phosphine phenyl groups removed for clarity.

The reaction of (**6**) and $Na[S_2CNMe_2]$ provides initially, a spectroscopically observable kinetic isomer $[Ru\{C(=C=CPh_2)SC(NMe_2)S\}(S_2CNMe_2)(CO)(PPh_3)]$ (**7k**) which slowly converts to the structurally characterised thermodynamic isomer (**7t**) (Fig. 1). [IR: 1936vs [ν(CO)], 1511s [ν(=C=C=C)], 1257m [ν(CS_2)] cm^{-1}. ^{1}H-NMR: δ 3.03, 3.22, 3.24, 3.29 [s × 4, 12 H, CH_3], 7.11, 7.25, 7.35, 7.47 [m × 4, 25 H, C_6H_5]. $^{13}C\{^1H\}$-NMR: δ 212.4 [C_β], 205.8 [S_2C], 201.3 [S_2C], 200.2 [d, RuCO, $J_{PC} = 14.0$], 139.4–125.6 [C_6H_5], 105.0 [d, RuCS, $J_{PC} = 10.8$ Hz], 103.0 [C_γ], 46.7, 44.1, 39.2, 38.9 [NCH_3] ppm. $^{31}P\{^1H\}$-NMR: δ 46.2 ppm. FAB-MS 822 [M]$^+$].

Crystal data for (**7t**): $C_{40}H_{37}N_2OPS_4Ru \cdot 2CHCl_3$, $M = 1060.7$, triclinic, space group $P\bar{1}$ (No. 2), $a = 11.897(2)$, $b = 12.262(1)$, $c = 17.208(2)$ Å, $\alpha = 98.74(1)$, $\beta = 92.73(1)$, $\gamma = 108.89(1)°$, $V = 2334.9(5)$ Å^3, $Z = 2$, $D_{calc.} = 1.509$ g cm^{-3}, μ(Mo–K$_\alpha$) = 0.93 mm^{-1}, $F(000) = 1076$. An orange prism of dimensions 0.93 × 0.27 × 0.17 mm was used. Independent reflections (8195) were measured (Siemens P4/PC diffractometer, graphite monochromated Mo–K$_\alpha$ radiation) at 203 K using ω scans. The structure was solved by direct methods and all the major occupancy non-hydrogen atoms were refined anisotropically using full-matrix least squares based on F^2 and absorption-corrected data to give $R_1 = 0.059$, and $wR_2 = 0.120$ [5568 observed reflections, $|F_o| > 4\sigma(|F_o|$, $2\theta \leq 50°$, 478 parameters].

The geometry at ruthenium is distorted octahedral with *cis* inter-ligand angles in the range 71.35(6)–94.6(2)°. The smallest of these involves the dithiocarbamate chelate [Ru–S(3) 2.460(2); Ru–S(4) 2.450(2) Å]. Dithiocarbamatoalkyl complexes involve 'folded envelope' metallacycles by virtue of the inclusion of an sp^3 carbon [2]. In contrast, the metallacycle in (**7t**) is essentially planar [max. dev.: 0.093Å by Ru] to satisfy the trigonality requirement at C(3) [angle sum 359.9°]. The pattern of bond lengths within the metallacycle [Ru–C(3) 2.089(6), C(3)–S(2) 1.799(6), S(2)–C(1) 1.735(6), C(1)–S(1) 1.701(6), S(1)–Ru 2.423(2) Å] conforms with the proposed valence bond description (Schemes 1 and 3). The allene unit comprises essentially equivalent bond lengths to C(4) [C(3)–C(4) 1.299(9), C(4)–C(5) 1.332(9) Å] subtending an angle of 175.6(7)°. The plane of the allene and its two C(5)-phenyl bonds is rotated 85° out of the Ru–C(3)–S(2) plane, torsional twists about the C(5)–C(11) and C(5)–C(17) bonds being 36 and 43°, respectively. The former orientation arises from the orthogonal π-systems at C(4) whilst the latter torsional twist indicates minimal conjugation between the aromatic and allene π-systems There are no significant inter or intra-molecular non-bonding interactions.

Dithiocarbamates are traditionally viewed as innocent spectator ligands. The above results however reveal facile participation in coupling reactions with unsaturated carbon-rich co-ligands. In this context, the recently reported insertion of 'nitrenes' into copper dithiocarbamates is relevant [8]. Furthermore, Roper's previously reported pyrrole-derived metallacycle is clearly related to those discussed above [9]. The presumed innocence of these previously tame ligands is thus further called into question.

Acknowledgements

Ruthenium salts were generously provided by Johnson Matthey Chemicals Ltd. A.F.H. gratefully acknowledges the award of a Senior Research Fellowship by The Royal Society and The Leverhulme Trust, and the financial support of the E.P.S.R.C.

References

[1] (a) I.R. Whittal, A.M. McDonagh, M.G. Humphrey, M. Samoc, Adv. Organomet. Chem. 42 (1998) 390. (b) I.R. Whittal, A.M. McDonagh, M.G. Humphrey, M. Samoc, Adv. Organomet. Chem. 43 (1998) 349. (c) N.J. Long, Angew. Chem. Int. Ed. Engl. 34 (1995) 826.

[2] D.J. Cook, K.J. Harlow, A.F. Hill, T. Welton, A.J.P. White, D.J. Williams, New. J. Chem. (1998) 311.

[3] (a) K.J. Harlow, A.F. Hill, T. Welton, A.J.P. White, D.J. Williams, Organometallics 17 (1998) 1916. (b) N.W. Alcock, I.D. Burns, K.S. Claire, A.F. Hill, Inorg. Chem. 31 (1992) 2906. (c) A.F. Hill, J.D.E.T. Wilton-Ely, Inorg. Synth. 33 (1999), in press.

[4] C. Slugovc, K. Mereiter, E. Zobetz, R. Schmid, K. Kirchner, Organometallics 15 (1996) 5275.

[5] J.P. Selegue, Organometallics 1 (1982) 217.

[6] (a) A.F. Hill, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 7, 1996, Pergamon Press, Oxford. Leading references include Ref. [5]. (b) T. Braun, P. Steinert, H. Werner, J. Organomet. Chem. 488 (1995) 169. (c) A. Fürstner, M. Picquet, C. Bruneau, P.H. Dixneuf, Chem. Commun. (1998), 1315. (d) M.P. Gamasa, J. Gimeno, C. Gonzalez-Bernardo, J. Borge, S. Garcia-Granda, Organometallics 16 (1997) 2483. (e) M.A. Esteruelas, A.V. Gómez, F.J. Lahoz, A.M. López, E. Oñate, L.A. Oro, Organometallics 15 (1996) 3423.

[7] A.J.P. White, D.J. Williams, unpublished results.

[8] G. Hogarth, A, Pateman, A. Sella, Chem. Commun. (1997) 1029.

[9] G.J. Irvine, C.E.F. Rickard, W.R. Roper, L.J. Wright, J. Organomet. Chem. 387 (1990) C9.