COMMUNICATION

Dalton
www.rsc.org/dalton

Novel palladium and platinum carbene-complexes containing dithiocarbonate ligand [M(PPh$_3$){η^2(*S*,*S*)-S$_2$CO]{C(SR)(NMe$_2$)}] formed *via* alkyl migration of *O*-alkyldithiocarbonate to thiocarbamoyl ligand †

Kuang-Hway Yih,*[a] Gene-Hsiang Lee[b] and Yu Wang[c]

[a] *Department of Applied Cosmetology, Hungkuang University, Shalu, Taichung, Taiwan 433, Republic of China*
[b] *Instrumentation Center, College of Science, National Taiwan University, Taiwan, Republic of China*
[c] *Department of Chemistry, National Taiwan University, Taiwan 106, Republic of China*

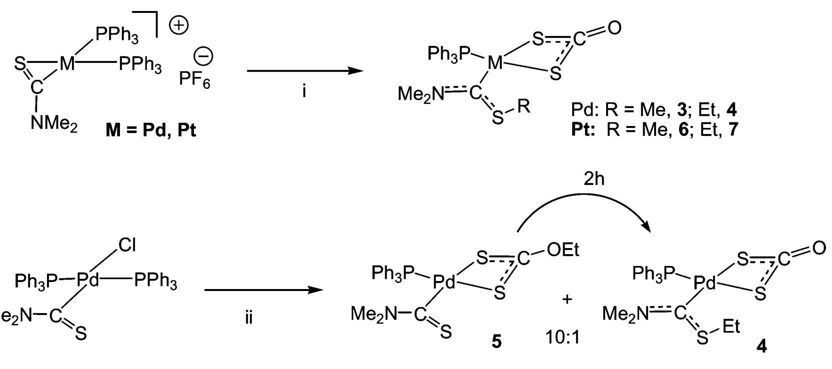
Received 13th May 2003, Accepted 18th June 2003
First published as an Advance Article on the web 24th June 2003

The first example of alkyl migration of *O*-alkyldithiocarbonate to thiocarbamoyl ligand results in carbene-complexes [M(PPh$_3$){η^2(*S*,*S*)-S$_2$CO]{C(SR)(NMe$_2$)}] (M = Pd, Pt; R = Me, Et) from the reactions of [M(η^2-SCNMe$_2$)(PPh$_3$)$_2$][PF$_6$] with KS$_2$COR in MeOH.

The activation of heteroallenes by transition metal complexes is a topic of much activity.[1] Formation of dithiocarbonate, S$_2$CO^{2-}, metal complexes from the reactions of metal carbonyl sulfide complexes with COS,[2] metal carbon disulfide complexes with dioxygen,[3] dealkylation,[4] iodide abstraction,[5] and hydrolysis[6] of *O*-alkyldithiocarbonate metal complexes have been reported. No alkyl migration process has been reported. As an extension of our investigation on the thio-metal and thiocarbamoyl palladium complexes,[7] herein, we report the unprecedented alkyl migration from the *O*-alkyldithiocarbonate ligand to thiocarbamoyl ligand in palladium and platinum complexes and crystal structure of the dithiocarbonate palladium carbene-complex.

The respective reactions of [Pd(η^2-SCNMe$_2$)(PPh$_3$)$_2$][PF$_6$] **1** and MeOCS$_2$K **2** or EtOCS$_2$K in methanol at room temperature yields the air-stable and orange–yellow complexes [Pd(PPh$_3$){η^2(*S*,*S*)-S$_2$CO]{C(SR)(NMe$_2$)}] (R = Me, **3**; Et, **4**) with 90 and 75% isolation yields (Scheme 1). Complexes **3** and **4** are isolated by recrystallization from hexane–CH$_2$Cl$_2$. The spectroscopic ‡ and analytical data of **3** and **4** were obtained. In the FAB mass spectra, base peaks with the typical Pd isotope distribution are in agreement with the [M]$^+$ molecular masses of **3** and **4**. The IR spectra of **3** and **4** show the C=O stretching band of the co-ordinated carbonate at 1675, 1603 and at 1681, 1605 cm^{-1}, respectively, which are indicative of a chelate dithiocarbonate ligand.[2,3,5,6] In the ^{1}H NMR spectrum of **3** and **4**, one resonance at δ 2.88 and three resonances at δ 1.20 and 3.45, 4.03 and the corresponding ^{13}C{^{1}H} NMR signals at δ 21.2, and at δ 13.4, 33.4 are attributed to the thiomethylene[8] and the thioethylene[8] groups respectively. From the above descriptions, it is clear that the alkyl group of the *O*-alkyldithiocarbonate ligand migrate to the thiocarbamoyl ligand forming dithiocarbonate palladium-carbene complexes. The π interaction between the carbene carbon and SR or NMe$_2$ and the higher chelate ability of the dithiocarbonate ligand than the *O*-alkyldithiocarbonate ligand are two important factors in stabilizing the carbene-complexes.

The aforementioned complex **3** has been studied by X-ray diffraction. ‡ An ORTEP plot of **3** is shown in Fig. 1. Crystals of **3** were obtained from diffusion of *n*-hexane into dichloromethane. In complex **3**, the palladium atom has a distorted square planar geometry. The palladium atom is displaced by 0.0396 Å from the least-squares plane. The distortion is mainly due to the short bite of the S$_2$CO^{-2} ligand, in which the S(1)–Pd–S(2) angle is 76.01(3)°. The carbene carbon and the three substitutents Pd, S, and N are coplanar to within 0.030 Å, and the bond angles about C(2) (126.7, 113.5, and 119.8°) clearly show the sp^2 character of the carbon. The Pd–C(2) bond distance, 2.043(4) Å, is longer than other Pd$^{\mathrm{II}}$–carbon-(carbonyl) distances,[9] and similar to those of Pd–C(carbene) distances.[9] Within the carbene, C(SMe)(NMe$_2$), ligand itself, the geometry is consistent with significant partial double bond character in the S(3)–C(2) and C(2)–N(1) bonds. Thus, the S(3)–C(2) bond distance (1.731(4) Å) is comparable to the C–S double bond in ethylenethiourea although it is longer than those in free CS$_2$ (1.554 Å). The C(2)–N(1) bond distance (1.308(4) Å) is typical for a C–N bond having partial double bond character and are certainly much shorter than the normal C–N (1.47 Å) single bond. This implies p$_\pi$–p$_\pi$ overlap, involving the empty p-orbital of the C(2) atom. The Pd–S(1) and Pd–S(2) bond distances of 2.3306(9) Å and 2.3250(9) Å are within the normal Pd–S length range (2.23 ~ 2.32 Å).[10] The Pd–S(1) bond



Scheme 1 Reagents and conditions: i, ROCS$_2$K, MeOH, r.t., 5 min, R = Me, 90%; Et, 75%. ii, EtOCS$_2$K, MeOH, r.t., 5 min.

---

† Electronic supplementary information (ESI) available: ^{1}H and ^{13}C{^{1}H} NMR spectra of **3** and the ^{1}H NMR spectrum of the mixtures of **4** and **5**. See http://www.rsc.org/suppdata/dt/b3/b305374a/

DOI: 10.1039/b305374a

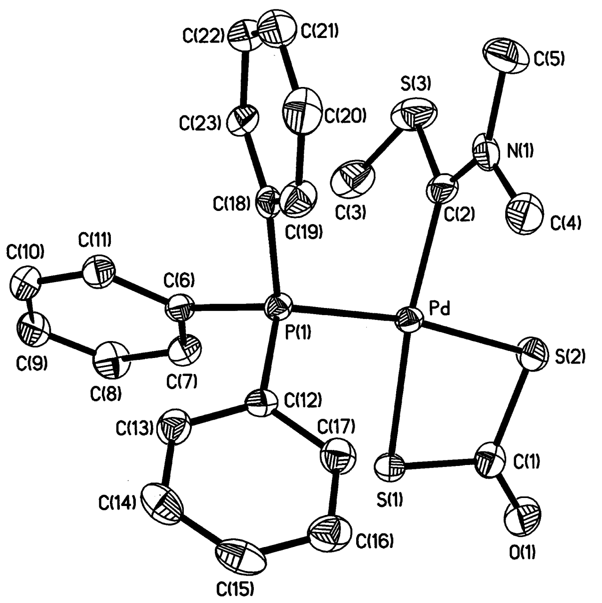


Fig. 1 ORTEP drawing with 50% thermal ellipsoids and atom-numbering scheme for the complex [Pd(PPh$_3$){η^2(*S*,*S*)-S$_2$CO}{C(SMe)-(NMe$_2$)}] **3**. Selected bond distances (Å) and angles (°) are as follows: Pd–C(2) 2.043(4), Pd–S(1) 2.3306(9), Pd–S(2) 2.3250(9), Pd–P(1) 2.2889(9), C(1)–O(1) 1.207(4), C(2)–S(3) 1.731(4), C(3)–S(3) 1.808(5), C(2)–N(1) 1.308(5); S(2)–Pd–P(1) 171.56(3), S(1)–Pd–C(2) 170.61(10), S(2)–C(1)–S(1) 108.0(2), N(1)–C(2)–Pd 126.7(3), C(5)–N(1)–C(4) 113.2(3).

distance is longer than the Pd–S(2) bond distance due to the high *trans* influence of carbene ligand than PPh$_3$ ligand. The bond distances within the dithiocarbonate ligand, S–C(av), 1.773(4) Å, and C(1)–O(1), 1.207(4) Å, fall in the range of values found for other dithiocarbonate complexes, and are indicative of an overall electronic delocalization within the S$_2$CO group.[2] The formation of an N, S-heteroatom carbene-complex from the intramolecular alkyl-thiocarbamoyl coupling is the first example in the literature.

In an attempt to get information about the alkyl migration, complex [Pd(η^1-CSNMe$_2$)(PPh$_3$)$_2$(Cl)][7] was used to react with EtOCS$_2$K in MeOH at room temperature for 5 min to form complexes [Pd(PPh$_3$){η^2(*S*,*S*)-S$_2$COEt]{η^1-CS(NMe$_2$)}] **5**‡ and **4** with a 10 : 1 ratio from the integration of ^{31}P{^{1}H} NMR spectrum. In the solution state, complex [Pd(PPh$_3$){η^2(*S*,*S*)-S$_2$COEt]{η^1-CS(NMe$_2$)}] **5** ethyl migration slowly gives **4** during 2 h. To test the generality of these reactions, we have studied the platinum system. Interestingly, the reactions of [Pt(η^2-SCNMe$_2$)(PPh$_3$)$_2$][PF$_6$] with KS$_2$COR (R = Me, Et) in MeOH at room temperature for 2 h also gave dithiocarbonate carbene-complexes [Pt(PPh$_3$){η^2(*S*,*S*)-S$_2$COR]{C(SR)(NMe$_2$)}] (R = Me, **6**; Et, **7**).‡ It is clear that in the reactions of thiocarbamoyl Pd and Pt complexes with KS$_2$COR (R = Me, Et) ligands, the intramolecular alkyl-thiocarbamoyl coupling reaction occurs. Olefin metathesis reactions of **3** and **4** are currently under investigation.

Acknowledgements

We thank the National Science Council of Taiwan, the Republic of China (project: NSC92-2113-241-001) for financial support and Mrs S.-L. Huang for carrying out NMR experiments.

Notes and references

‡ *Selected spectroscopic data*: ^{1}H (500 MHz) and ^{13}C{^{1}H} (125 MHz) NMR (CDCl$_3$, relative to SiMe$_4$, multiplicity, assignment, *J* in Hz) ^{31}P{^{1}H} (202 MHz) NMR (H$_3$PO$_4$ external standard). **3**: IR (KBr) *ν*CO/cm^{-1}: 1675(vs), 1603(vs), ν_{as}CS: 832(m). ^{1}H NMR: *δ* 2.88 (s, 3H, SCH_3), 2.96, 3.52 (s, 6H, 2NCH_3), 7.30–7.57 (m, 15H, Ph). ^{31}P{^{1}H} NMR: *δ* 28.0 (PPh$_3$). ^{13}C{^{1}H} NMR: *δ* 21.2 (s, SCH$_3$), 43.6, 52.0 (s, NCH$_3$), 128.2–134.2 (m, C of Ph), 199.0 (s, S$_2$$C$O), 247.9 (d, N$C$SMe, $J_{P–C}$ = 14.6). MS (FAB, NBA, *m*/*z*): 564 (M$^+$). Anal. Calcd. for C$_{23}$H$_{24}$NOPS$_3$Pd: C, 48.98; H, 4.30; N, 2.48%. Found: C, 49.85; H, 4.56; N, 2.38. **4**: IR (KBr) *ν*CO/cm^{-1}: 1681(vs), 1605(vs), ν_{as}CS: 832(m). ^{1}H NMR: *δ* 1.20 (t, 3H, SCH$_2$CH_3, $J_{H–H}$ = 7.5), 2.89, 3.54 (s, 6H, 2NCH_3), 3.45, 4.03 (m, 2H, SCH_2), 7.40–7.57 (m, 15H, Ph). ^{31}P{^{1}H} NMR: *δ* 28.0 (PPh$_3$). ^{13}C{^{1}H} NMR: *δ* 13.4 (s, SCH$_2$$CH_3$), 33.4, (s, S$CH_2$), 43.6, 52.2 (s, N$CH_3$), 128.4–134.0 (m, C of Ph), 199.1 (s, S$_2$$C$O), 246.7 (d, N$C$SEt, $J_{P–C}$ = 15.2). MS (FAB, NBA, *m*/*z*): 578 (M$^+$). Anal. Calcd. for C$_{24}$H$_{26}$NOPS$_3$Pd: C, 49.87; H, 4.53; N, 2.42%. Found: C, 50.15; H, 4.38; N, 2.28.

Crystal data for (**2**)$_2$·CH$_3$CN: C$_6$H$_9$K$_2$NO$_2$S$_4$, *M* = 333.58, monoclinic, space group $P2_1/n$, a = 9.91767(7) Å, b = 10.3027(8) Å, c = 14.3530(11) Å, β = 99.660(2)°, V = 1445.77(19) Å^3, Z = 4, D_{calcd} = 1.533 g cm^{-3}, μ = 1.214 mm^{-1}, independent reflections 3318, θ_{range} = 2.32–27.50°. Total number of parameters: 136. R = 0.028, R_w = 0.067; GOF = 1.038, Mo Kα radiation; λ = 0.71073 Å; T = 150(1) K; ΔF = 0.474, −0.190 e Å^3. *Crystal data* for **3**: C$_{23}$H$_{24}$NOPPdS$_3$, *M* = 563.98, monoclinic, space group $P2_1/c$, a = 16.3638(2) Å, b = 9.3374(1) Å, c = 15.7117(2) Å, β = 98.2957(6)°, V = 2375.56(5) Å^3, Z = 4, D_{calcd} = 1.577 g cm^{-3}, μ = 1.128 mm^{-1}, independent reflections 5458, θ_{range} = 1.26–27.50°. Total number of parameters: 272. R = 0.039, R_w = 0.090; GOF = 1.119, Mo Kα radiation; λ = 0.71073 Å; T = 150(1) K; ΔF = 0.813, −0.728 e Å^3. Absorption corrections of **2** and **3** have been carried out. The two structures were solved by Patterson synthesis and then refined *via* standard least-squares and difference Fourier techniques. Non-hydrogen atoms were refined by using anisotropic thermal parameters. CCDC reference numbers 210481 and 210482. See http://www.rsc.org/suppdata/dt/b3/b305374a/ for crystallographic data in CIF or other electronic format.

5: IR (KBr) *ν*CS/cm^{-1}: 1436(m). ^{1}H NMR: *δ* 1.40 (t, 3H, OCH$_2$CH_3, $^3J_{H–H}$ = 7.0), 2.95, 3.30 (s, 6H, NCH$_3$), 4.55 (m, 2H, OCH_2CH$_3$), 7.37–7.62 (m, 15H, Ph). ^{31}P{^{1}H} NMR: *δ* 24.8 (br, PPh$_3$). ^{13}C{^{1}H} NMR: *δ* 13.8 (s, OCH$_2$$CH_3$), 38.9, 40.8 (s, NCH$_3$), 67.8, 68.0 (s, O$CH_2CH_3$), 128.3–134.2 (m, Ph), 210.0 (s, OCS$_2$), 233.2 (s, NCS). MS (FAB, NBA, *m*/*z*): 578 (M$^+$). **6**: IR (KBr) νCO/cm^{-1}: 1683(vs), 1610(vs). ^{1}H NMR: *δ* 2.82 (s, 3H, SCH_3), 2.93, 3.49 (s, 6H, 2NCH_3), 7.28–7.76 (m, 15H, Ph). ^{31}P{^{1}H} NMR: *δ* 15.4 (t, PPh$_3$, $J_{Pt–P}$ = 1662.3). ^{13}C{^{1}H} NMR: *δ* 21.8 (t, SCH$_3$, $J_{Pt–C}$ = 34.5), 43.2, 51.2 (t, NCH$_3$, $J_{Pt–C}$ = 17.5, 30.8), 128.1–137.2 (m, C of Ph), 195.5 (s, S$_2$$C$O), 229.8 (d, N$C$SMe, $J_{P–C}$ = 9.5). MS (FAB, NBA, *m*/*z*): 653 (M$^+$). Anal. Calcd. for C$_{23}$H$_{24}$NOPS$_3$Pt: C, 42.32; H, 3.71; N, 2.15%. Found: C, 42.48; H, 3.80; N, 2.01. **7**: IR (KBr) *ν*CO/cm^{-1}: 1680(vs), 1612(vs). ^{1}H NMR: *δ* 1.43 (t, 3H, SCH$_2$CH_3, $J_{H–H}$ = 7.1), 2.94, 3.21 (s, 6H, 2NCH_3), 4.55 (q, 2H, SCH_2, $J_{H–H}$ = 7.1), 7.37–7.86 (m, 15H, Ph). ^{31}P{^{1}H} NMR: *δ* 28.0 (t, PPh$_3$, $J_{Pt–P}$ = 1616). ^{13}C{^{1}H} NMR: *δ* 13.7 (t, SCH$_2$$CH_3$, $J_{Pt–C}$ = 47.1), 39.8 (t, SCH$_2$, $J_{Pt–C}$ = 17.4), 43.8, 51.8 (t, NCH$_3$, $J_{Pt–C}$ = 17.4, 32.4), 128.2–134.4 (m, C of Ph), 194.4 (s, S$_2$$C$O), 226.5 (d, N$C$SEt, $J_{P–C}$ = 9.2). MS (FAB, NBA, *m*/*z*): 667 (M$^+$). Anal. Calcd. for C$_{24}$H$_{26}$NOPS$_3$Pt: C, 43.23; H, 3.93; N, 2.10%. Found: C, 43.35; H, 4.08; N, 2.02.

1 M. Schmittel, D. Rodriguez and J. P. Steffen, *Angew. Chem. Int. Ed.*, 2000, **39**, 2152 and references therein. K. Aparna, R. McDonald and R. G. Cavell, *J. Am. Chem. Soc.*, 2000, **122**, 9314 and references therein. L. D. Field, W. J. Shaw and P. Turner, *Organometallics*, 2001, **20**, 3491 and references therein.
2 T. R. Gaffney and J. A. Ibers, *Inorg. Chem.*, 1982, **21**, 2860; H. Werner, W. Bertleff, B. Zimmer-Gasser and U. Schubert, *Chem. Ber.*, 1982, **115**, 1004; T. R. Gaffney and J. A. Ibers, *Inorg. Chem.*, 1982, **21**, 2851; C. Bianchini, A. Meli and A. Orlandini, *Inorg. Chem.*, 1982, **21**, 4166.
3 F. Cecconi, C. A. Ghilardi, S. Midollini, S. Moneti, A. Orlandini and G. Scapacci, *J. Chem. Soc., Dalton Trans.*, 1989, 211; C. Bianchini, C. A. Ghilardi, A. Meli and A. Orlandini, *J. Organomet. Chem.*, 1985, **286**, 259; C. Bianchini and A. Meli, *J. Chem. Soc., Dalton Trans.*, 1983, 2419; C. Bianchini and A. Meli, *Inorg. Chem.*, 1987, **26**, 4268; C. Bianchini, C. Mealli, A. Meli and M. Sabat, *J. Chem. Soc., Chem. Commun.*, 1985, 1024.
4 R. Colton, J. C. Traeger and V. Tedesco, *Inorg. Chim. Acta*, 1993, **210**, 193; R. Colton and V. Tedesco, *Inorg. Chim. Acta*, 1992, **202**, 95; R. Colton and V. Tedesco, *Inorg. Chim. Acta*, 1991, **183**, 161.
5 J. Doherty, J. Fortune, A. R. Manning and F. S. Stephens, *J. Chem. Soc., Dalton Trans.*, 1984, 1111.
6 R. Rossi, A. Marchi, L. Margon, U. Casellato and R. Graziani, *J. Chem. Soc., Dalton Trans.*, 1990, 2923.
7 K. H. Yih, G. H. Lee and Y. Wang, *Inorg. Chem. Commun.*, 2003, **6**, 577; K. H. Yih, G. H. Lee and Y. Wang, *Inorg. Chem. Commun.*, 2003, **6**, 213; K. H. Yih, G. H. Lee and Y. Wang, *Inorg. Chem.*, 2003,

42, 1092; K. H. Yih, G. H. Lee, S. L. Huang and Y. Wang, *Organometallics*, 2002, **21**, 5767.

8 K. H. Yih, Y. C. Lin, M. C. Cheng and Y. Wang, *J. Chem. Soc., Chem. Commun.*, 1993, 1380; K. H. Yih, Y. C. Lin, M. C. Cheng and Y. Wang, *J. Chem. Soc., Dalton Trans.*, 1995, 1305.

9 D. J. Cardin, B. Cetinkaya and M. F. Lappert, *Chem. Rev.*, 1972, **72**, 545 and references cited therein. W. M. Butler and J. H. Enemark, *Inorg. Chem.*, 1973, **12**, 451; O. P. Anderson and A. B. Packard, *Inorg. Chem.*, 1978, **17**, 1333; R. D. Wilson, K. Kamitori, H. Ogoshi, Z. Yoshida and J. A. Ibers, *J. Organomet. Chem.*, 1979, **173**, 199.

10 H. L. Bozec, P. H. Dixneuf, A. J. Carty and N. J. Taylor, *Inorg. Chem.*, 1978, **17**, 2568.