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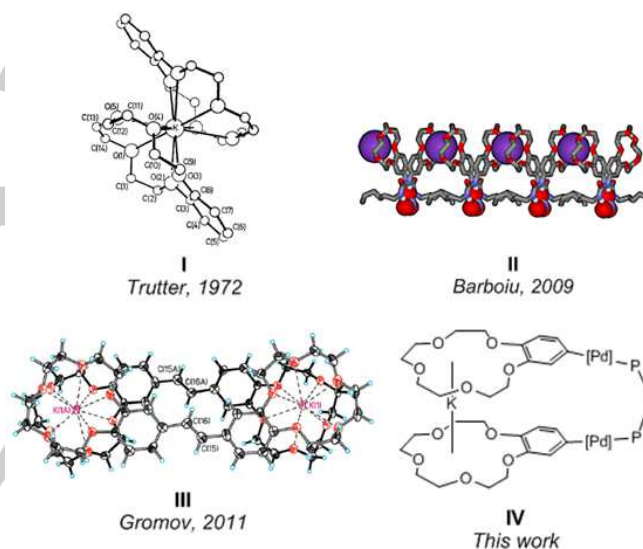
Dinuclear crown ether palladium complex: a highly effective strategy for encapsulating potassium cations in small crown ether rings

Fátima Lucio–Martínez^[a], Brais Bermúdez^[a], Juan M. Ortigueira^[a], Harry Adams^[a], Alberto Fernández^[b], M. Teresa Pereira^[a] and José M. Vila^{*[a]}

The potential of 15-crown-5 ethers to link rather large cations as potassium is limited to the quasi parallel arrangement of two oxygen donor moieties upon appropriate orientation of the corresponding ether ring containing molecules. Substrates bearing the two crown ethers capable of achieving such coordination are hitherto unknown. The synthesis and isolation of a tailored-made dinuclear palladacycle bearing 15-crown-5 ether rings on the metallated phenyls offers such a possibility providing the adequate environment for the formation of the sandwiched $[K(\text{metallacycle-15-crown-5})_2]$ moiety. This synthetic strategy culminates also in isolation of the first palladacycle able to entrap potassium cation through bonding to two 15-crown-5 ether rings in a single molecule.

Crown ethers are ligands well known for their selectivity towards encapsulating metal ions, especially those of the alkaline and alkaline-earth metals, for which cavity size is a paramount factor.¹ Hence, they have shown a wide variety of applications related to sensors, membrane ion transport or potential anti-cancerous species, among others.² On the other hand, cyclometalated compounds also display interesting properties as metallomesogens,³ in catalysis⁴ and as antineoplastic substances.⁵ Since the first cyclometallated compound bearing a crown-ether functionality was synthesized in 2001 by Bezoudnova *et al.*⁶ much work has been done in this field in order to combine both species.⁷ We ourselves have indulged in the preparation of crown-ether palladacycles and we have shown that in accordance with the ring size sodium^{8a} and silver^{8b} cations may be accommodated in 15-crown-5 and in 18-crown-6 rings, respectively. The potassium cation is amongst those that show great affinity for crown-ether rings and for which more studies have been carried out. Its size makes it most suitable for 18-crown-6 rings; for the smaller 15-crown-5 ether a sandwiched-type geometry has been suggested for complexation of the cation by two 15-crown-5 ether moieties.^{9,10} To date a rather significant quantity of references may be found related to this sort of arrangement. Then, the crown ether may serve as an entrapping agent for K^+ ,¹¹ to sustain K^+ as the counter-ion,¹² and for making bis-sandwiched tetracrown complexes.¹³ In Scheme 1 some relevant examples are depicted

which show **I** the seminal potassium 1:2 complex by Truter *et al.*,^{14a} **II** the polymeric structure where K^+ cations and NO_3^- anions form connecting bridges with crystal packing being responsible for the sandwiched geometry,^{14c} and **III** the self-assembly of bis(crown)stilbenes. Nevertheless, it should be noted that alkali metal-crown ether interactions exceed simplistic "size fit" considerations.^{14b} Likewise, related sandwich structures with metals other than potassium have also appeared: In,^{15a} Sn,^{15b} Dy,^{15c} also, other claims to potassium 15-crown-5 coordination albeit lacking clear crystallographic evidence have appeared.¹⁶



Scheme 1. Examples of isolated complexes containing the potassium cation coordinated by separate molecules, **I**, **II**, **III**; and coordinated in a single molecule, **IV**.

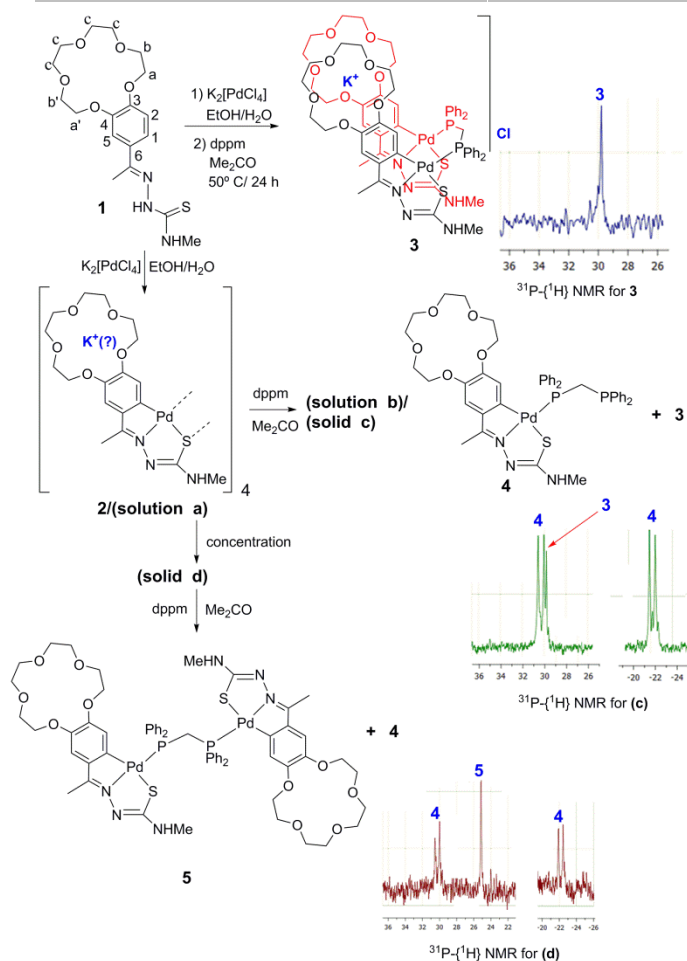
At variance with the hitherto known examples we sought out to prepare the first species containing the two coordinated crown rings in one single molecule **IV**. Thus, following our previous results concerning crown-ether palladacycles we became interested in trying to devise a convenient palladacycle featuring the two 15-crown-5 ethers needed for K^+ coordination in the possibility of synthesizing a mixed potassium sandwiched-palladium complex. We anticipated that tetranuclear thiosemicarbazone palladacycles¹⁷ could offer an advantageous solution towards the isolation of the aforesaid potassium coordination with 15-crown-5 moieties on the four metallated phenyl rings. Then, our ensuing hypothesis was that adequately separating the two pairs of parallel metallated moieties should produce the needed arrangement giving molecules appropriate for sandwiched potassium coordination; accordingly, what follows is our synthetic strategy for the systematic coordination of the bulky K^+ cation to 15-crown-5 ethers *via* thiosemicarbazone palladacycles.

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Scheme 2. Reaction sequence leading to the synthesis of the sandwiched potassium crown ether complex.

A suitable metal salt was chosen in pursuit of achieving in one single reaction a palladacycle with the K^+ cation coordinated to 15-crown-5 ether. Hence, 3,4-($C_8H_{16}O_5$) $C_6H_3C(Me)=N-N(H)C(=S)NHMe$, **1**, was treated with $K_2[PdCl_4]$ in ethanol to give a yellow precipitate which was filtered off and the mother liquor **a** set aside. The solid was too insoluble for NMR characterization, therefore, assuming it to be the tetranuclear cluster, **2**, inclusive or not of coordinated potassium, it was treated with $Ph_2PCH_2PPh_2$ (dppm) in slight excess of a 1:4 ratio which gave a clear yellow solution **b**.

Work up of the solution gave a solid, **c**, for which the $^{31}P\{-^1H\}$ NMR data showed a pair of doublets centered at 30.3 and -22.1 ppm ($^2J = 69.3$ Hz) and a singlet at 29.8 ppm. Reducing the initial mother liquor **a** to low volume gave a precipitate, **d**, which was also reacted with dppm in a similar fashion; the $^{31}P\{-^1H\}$ NMR was analogous to **c**, albeit the singlet was centered at 25.0 ppm; in both cases the pair of doublets was the major product. Attempts to recrystallize **c** gave suitable crystals of **3** for an X-ray analysis (*vide infra*); the $^{31}P\{-^1H\}$ NMR spectrum for **3** showed only a sharp singlet at 29.8 ppm. We then tentatively assigned the two doublets in the spectrum of **d** to compound **4** and the singlet at 25.0 ppm to **5**, presumably lacking the potassium cation. Attempts to separate the compounds derived from **d** were not conducted; however, in order to assert their formation and to verify the spectroscopic assignments we then treated ligand **1** with a potassium-free salt, $PdCl_2$, and after work up and addition of dppm pure **4** and **5** could be obtained.

Therefore, the presence of these species void of K^+ in the initial procedure would be in agreement with our assumption that K^+ only coordinates to 15-crown-5 ethers in a sandwiched arrangement. Furthermore, treatment of compound **4** with potassium chloride only gave the starting material; no potassium coordination was observed. The measured % of potassium in **2**, albeit low, was enough to produce a small percentage of **3** in the mixture **3** + **4**, and this prompted us to devise a preparation of pure **3**, after which we obtained, again, the single crystals as definite proof. Our synthetic strategy for the isolation of a sandwiched K^+ was predicated on the adequate phosphine ratio. This route led to reaction of the aforementioned yellow precipitate with $Ph_2PCH_2PPh_2$ (dppm) in 1:2 ratio, in acetone at $50^\circ C$ for 24 h. The resulting orange solution was reduced to low volume and the solid formed was filtered off. A diagnostic feature of complex **3** was its singlet at 29.8 ppm in the $^{31}P\{-^1H\}$ NMR spectrum in deuterated acetone, assigned to the two equivalent phosphorus nuclei. Also, the % of potassium was in accordance with the presence of the cation in **3**.

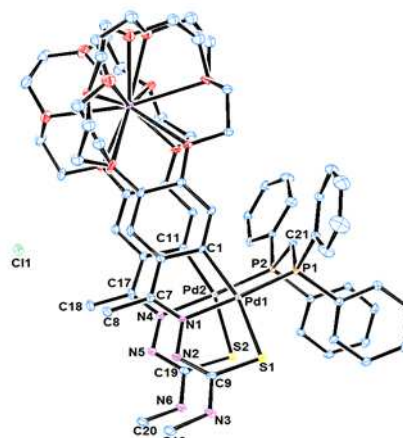


Figure 1. Thermal ellipsoid plot of **3** shown at the 30% probability level. Hydrogen atoms and minor disorder components have been omitted for clarity. Selected bond distances (Å) and angles (deg) for **3**: Pd1–N1 2.029(3), Pd1–C1 2.045 (4), Pd1–P1 2.2563 (13), Pd1–S1 2.3678 (13), Pd2–N4 2.036 (3), Pd2–C11 2.040 (4), Pd2–P2 2.2600 (13), Pd2–S2 2.3578 (12), N1–Pd1–C1 80.53(14), C1–Pd1–P1 96.62(11), N1–Pd1–S1 81.83(9), P1–Pd1–S1 101.12(4), N4–Pd2–C11 80.57(15), C11–Pd2–P2 95.97 (12), N2–Pd2–S2 81.63(10), P2–Pd2–S2 101.84(4).

The IR spectrum and the 1H NMR spectrum showed absence of the $\nu(N-H)$ stretch and of the hydrazinic proton resonance, respectively, consistent with $NH_{hydrazinic}$ deprotonation. Furthermore, the C1 resonance in the ^{13}C NMR spectrum was low-field shifted upon metallation.¹⁸ The *a* and *b* methylene proton resonances, and the *H2* resonance were high-field shifted compared to the related values detected for **1** due to the proximity of the phosphine phenyl groups; the latter resonance was coupled to ^{31}P .

Recrystallization from acetone again gave single crystals confirming the structure and the reproducibility of the preparation routine. The crystal structure of complex **3** gives definite proof of binding of the bulky K^+ to a 15-crown-5 ether by encapsulating the cation between two ether rings of the molecule (Figure 1); a breakthrough in palladacycle chemistry. The bond distances and angles in the cyclometallated part are within the expected values with allowance for lengthening of the Pd(1)–N(1) and Pd(2)–N(4) bond lengths consequent on the *trans* influence of the phosphine ligand. The O–K bond distances are all different from one another in the non-centrosymmetric structure ranging from 2.65–3.01 Å; although these data are similar to others found in

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related K^+ 15-crown-5-ether compounds,¹³ five bond lengths are significantly shorter than those observed earlier.^{14a,14c} The two halves of the molecule are close to parallel: the planes formed by the oxygen atoms ca. 2.6°, and the palladium coordination planes ca. 9.08°. Slipped π - π stacking interactions between the two palladacycle moieties, *i.e.*, the phenyl, metallacycle and coordination-*N,S* rings most surely contribute to the stabilization of the structure with centroid distances ranging from 3.54–3.69 Å.^{8b,19}

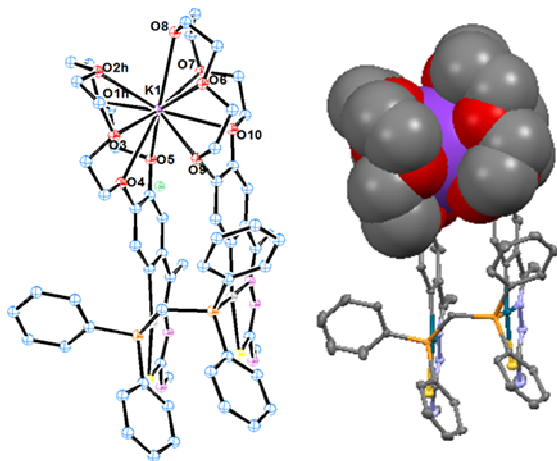


Figure 2. (a) Thermal ellipsoid plot of **3** shown at the 30% probability level along the *b* axis. (b) Space-filling model for the sandwich coordination in **3**.

In summary, we have isolated a unique dinuclear phosphine-bridged thiosemicarbazone palladacycle containing 15-crown-5 ether rings on the metallated phenyls, capable of coordinating to the K^+ cation by sandwiching it between the two ether rings, which results in a trinuclear mixed main group-transition metal complex. This result represents a further enrichment in the chemistry of palladacycles as well as in the coordination chemistry of crown ethers; the crystal structure representing unambiguous evidence of a palladium crown ether metallacycle capable of bonding to the K^+ cation and constitutes the cornerstone for a systematic method for encapsulating bulky cations to relatively small ether rings. Further studies regarding this chemistry are presently underway.

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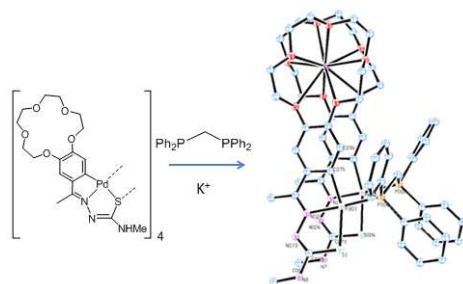
Keywords: Crown-compounds, Palladacycle, Potassium, Sandwich-complexes.

[1] C. J. Pedersen; *J. Am. Chem. Soc.*; **1967**, *89*, 7017-7036.

[2] (a) C. Preihs, D. Magda, J. Sessler, *J. Porphyrins and Phthalocyanines*, **2011**, *15*, 539-546. (b) Z. Sun, M. Barboiu, Y.-M. Legrand, E. Petit, A. Rotaru, *Angew. Chem. Int. Ed.* **2015**, *54*, 14473-14477. (c) A. Gilles, M. Barboiu *J. Am. Chem. Soc.* **2016**, *138*, 426-432. (d) Z. Sun, A. Gilles, I. Kocsis, Y.-M. Legrand, E. Petit, M. Barboiu, *Chem. Eur. J.*, **2016**, *22*,

2158-2164. (e) S. D. Alexandratos, C. L. Stine, *React. Funct. Polym.*, **2004**, *60*, 3-16. (f) S. Kado, Y. Takeshima, Y. Nakahara, K. Kimura, *J. Incl. Phenom. Macrocycl. Chem.*, **2012**, *72*, 227-232. (g) H.-R. Yu, J.-Q. Hu, X.-H. Lu, X.-J. Ju, Z. Liu, R. Xie, W. Wang, L.-Y. Chu, *J. Phys. Chem. B.*, **2015**, *119*, 1696-1705.

- [3] (a) M. Marcos, in *Metallomesogens. Synthesis, Properties and Applications*, ed. J. L. Serrano, VCH, Weinheim, 1996. (b) D. Pucci, G. Barneiro, A. Bellusci, A. Crispini, M. Ghedini, *J. Organomet. Chem.* **2006**, *691*, 1138-1142. (c) M.L.S Lowry, S. Bernhard, *Chem. Eur. J.* **2006**, *12*, 7970-7977.
- [4] (a) J. Dupont, M. Pfeffer, J. Spencer, *Eur. J. Inorg. Chem.*; **2001**, 1917-1927. (b) J. Dupont, C. S. Consorti, J. Spencer, *Chem. Rev.* **2005**, *105*, 2527-2571. (c) S. Doherty, J. G. Knight, N. A. B. Ward, D. M. Bittner, C. Wills, W. McFarlane, W. Clegg, R.W. Harrington, *Organometallics* **2013**, *32*, 1773-1788.
- [5] (a) C. Navarro-Ranninger, I. López-Solera, V. M. González, J. M. Pérez, A. Álvarez-Vales, A. Martín, P. Raithby, J. R. Masaguer, C. Alonso, *Inorg. Chem.*; **1996**, *35*, 5181-5187. (b) A. Habtemariam, B. Watchman, B. S. Potter, R. Palmer, S. Parsons, A. Parkin, P. J. Sadler, *J. Chem. Soc. Dalton Trans.* **2001**, 1306-1318. (c) A. Gómez-Quiroga, C Navarro-Ranninger, *Coord. Chem. Rev.* **2004**, *248*, 119-133. (d) J. Ruiz, J. Lorenzo, L. Sanglas, N. Cutillas, C. Vicente, M. D. Villa, F. X. Avilés, G. López, V. Moreno, J. Pérez, D. Bautista, *Inorg. Chem.* **2006**, *45*, 6347-6360. (e) P. Chellan, S. Nasser, L. Vivas, K. Chibale, G. S. Smith, *J. Organomet. Chem.*; **2010**, *695*, 2225-2232.
- [6] E. Y. A. Bezoudnova, D. Ryabov, *J. Organomet. Chem.*; **2001**, *622*, 38-42.
- [7] (a) S. Coco, C. Cordovilla, P. Espinet, J.-L. Gallani, D. Guillon, B. Donnio, *Eur. J. Inor. Chem.* **2008**, 1210-1218. (b) J. Arias, M. Bardaji, P. Espinet, *J. Organomet. Chem* **2006**, *691*, 4990-4999.
- [8] (a) S. Castro-Juiz, A. Fernández, M. López-Torres, D. Vázquez-García, A. J. Suárez, J. M. Vila, J. J. Fernández, *Organometallics*, **2009**, *28*, 6657-6665. (b) D. Vázquez-García, A. Fernández, M. López-Torres, A. Rodríguez, A. Varela, M. T. Pereira, J. M. Vila, J. J. Fernández, *Organometallics*, **2011**, *30*, 396-404.
- [9] B. Dietrich, P. Viout, J-M Lehn, *Macrocyclic Chemistry – Aspects of Organic and Inorganic Supramolecular Chemistry* VHC New York, 1993, 174.
- [10] C. J. Pedersen, *J. Am. Chem. Soc.* **1970**, *92*, 386-391.
- [11] J. C. Peters, A. L. Odom, C. C. Cummins, *Chem. Commun.*, **1997**, 1995-1996.
- [12] (a) C.-Y. Lin, J. C. Fettinger, N. F. Chilton, A. Formanuk, F. Grandjean, G. J. Long, P. P. Power, *Chem. Commun.*, **2015**, *51*, 13275-13278. (b) D. M. King, J. McMaster, F. Tuna, E. J. L. McInnes, W. Lewis, A. J. Blake, S. T. Liddle, *J. Am. Chem. Soc.* **2014**, *136*, 5619-5622. (c) J. Liu, J.-H. Zhang, D.-Q. Wang, J.-M. Dou, *Acta Cryst.* **2005**, **E61**, m1652. (d) S. T. Liddle, W. Clegg, *J. Chem. Soc., Dalton Trans.*, **2001**, 3549-3550.
- [13] S. P. Gromov, A.I. Vedernikov, N. A. Lobova, L. G. Kuz'mina, S. S. Basok, Y. A. Strelenko, M.V. Alfimov, J.A. K. Howard, *New J. Chem.*, **2011**, *35*, 724-737.
- [14] (a) P. R. Mallinson, M. R. Truter, *J. Chem Soc. Perkin II*, **1972**, 1818-1823. (b) J. Han, N. Song, X. Tian, X. Zhen, S. Liu, *J Incl Phenom Macrocycl Chem.*, **2013**, *77*, 301-308. (c) A. Cazacu, Y. M. Legrand, A. Pasc, G Nasr, A. Van der Lee, E. Mahon, M. Barboiu, *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 8117-8122.
- [15] (a) B. F. T. Coper, C. L. B. Macdonald, *J. Organomet. Chem.*, **2008**, *693*, 1707-1711. (b) C. Beattie, P. Farina, W. Levison, G. Reid, *Dalton Trans.*, **2013**, *42*, 15183-15190. (c) Y-S. Ding, T. Han, Y-Q. Hu, M. Xu, S. Yang, Y-Z. Zheng, *Inorg. Chem. Frontiers*, **2016**, *3*, 798-807.
- [16] J. Arias, M. Bardaji, P. Espinet, *Inorg. Chim. Acta.* **2011**, *365*, 501-504 (b) S. Inokuma, T. Funaki, S-I Kondo, J. Nishimura, *Tetrahedron*, **2004**, *60*, 2043-2050.
- [17] (a) J. M Vila, M. T. Pereira, A. Fernández, M. López-Torres, H. Adams, *J. Chem. Soc.; Dalton Trans.*; **1999**, 4193-4201. (b) J. M. Antelo, L. Adrio, M. T. Pereira, J. M. Origueira, J. J. Fernández, J. M Vila, *Crystal Growth & Design*, **2010**, *18*, 700-708.
- [18] J. M. Vila, M. Gayoso, M. T. Pereira, M. López, G. Alonso, J. J. Fernández *J. Organomet. Chem.*, **1993**, *445*, 287-294.
- [19] C. Janiak, *J. Chem. Soc. Dalton Trans.* **2000**, *21*, 3885-389.



Design of a palladacycle for coordinating K⁺ via sandwich disposition

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421–424

A doubly 15-crown-5 ether functionalized palladacycle is extremely efficient for achieving potassium coordination via a sandwich assembly. A strategy for the synthesis is devised to obtain a homobimetallic phosphine-bridged palladium organometallic comprising the two oxygen donor moieties within one molecule, in a quasi-parallel orientation of the 15-crown-ether rings.

Dinuclear crown ether palladium complex: a highly effective strategy for encapsulating potassium cations in small crown ether rings

A crown palladacycle sandwiching potassium