Supplementary Material (ESI) for Dalton Transactions


# Electronic Supplementary Information for B618567C

## Tetranuclear palladium complexes with benzoquinonediimine ligands: synthesis, molecular structure and electrochemistry

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### Synthesis and characterization of compound 11

Similarly to the procedure described for the synthesis of analogs except for the reaction time which was only 2 h, the tetraamidobenzene derivative $C_6H_2[NC(O)CH_2t\text{-}Bu]_4$ precursor (0.23 mmol, 0.110 g) was reduced with $LiAlH_4$ in THF. After the aerobic work-up, the crude product was directly reacted with $[Pd(acac)_2]$ (1.00 mmol, 0.300 g) in toluene. The residue was then redissolved in dry dichloromethane, and the solution was filtered through Celite and purified by silica gel chromatography, affording **11**.
Yield : 0.012 g (6%). $^1$H NMR (300 MHz, $CDCl_3$, 298 K) δ:1.02 (s, 9 H, $CH_3$), 1.03 (s, 9 H, $CH_3$), 1.07 (s, 9 H, $CH_3$), 1.36 (s, 9 H, amidic $CH_3$), 1.89 (s, 3 H, $CH_3$acac), 1.95 (s, 3 H, $CH_3$acac), 1.96 (s, 3 H, $CH_3$acac), 1.97 (s, 3 H, $CH_3$acac), 2.90 (br s with sh, 6 H, $CH_2$), 5.25 (br s, 1 H, N⋯C⋯C–H), 5.30 (s, 1 H, O⋯C⋯C–H), 5.33 (s, 1 H, O⋯C⋯C–H), 5.60 (br s, 1 H, N⋯C⋯C–H). ESMS: *m/z*: 841 $[M+1]^+$. UV-vis ($CH_2Cl_2$): λ (nm) (ε) 341 (9300), 431 (20300), 456 (27900), 494 (34000), 637 (2000).
The $^1$H NMR spectrum of **11** contains three signals at 1.02, 1.03 and 1.07 ppm and a signal at 1.36 ppm corresponding to the methyl groups of the N-$CH_2$-*t*-Bu moities and of the amido function, respectively (Fig. S1). In addition, the four non-equivalent methyl groups of the ancillary acac ligands appear as four singlets in the range 1.89 – 1.96 ppm and confirm that **11** is unsymmetrical.

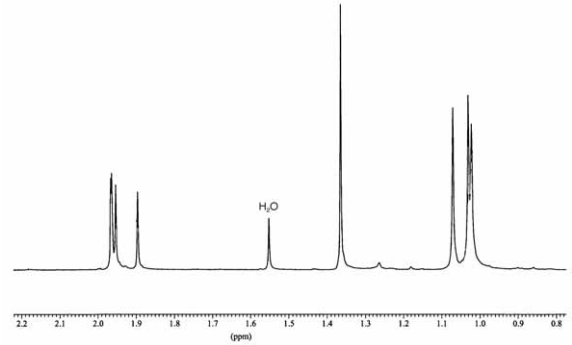


**Fig. S1** $^1$H NMR spectrum of **11** in $CDCl_3$ in the region of the methyl signals.

The electrospray mass spectrum shows a molecular peak at 841 $[M+1]^+$ consistent with the formation of **11**. Crystals suitable for X-ray analysis could be obtained from a mixture $CH_2Cl_2$/*n*-hexane allowing the determination of the molecular structure **11**.
A crystallographic disorder of the carbonyl group in **11** which occupies 25% of each α-position to the nitrogen atoms was revealed (Fig. S2).

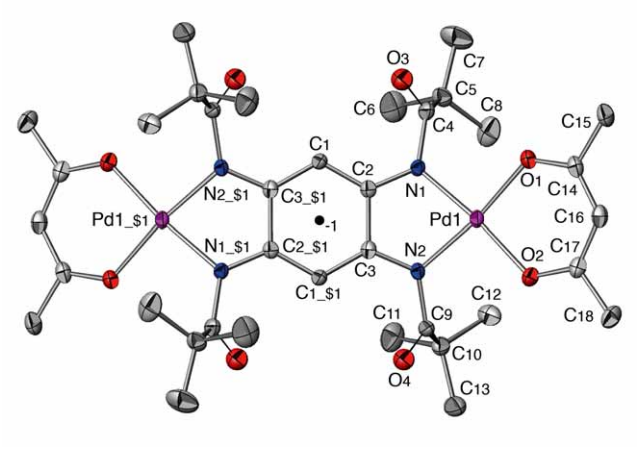


**Fig. S2** ORTEP view of complex **11** with partial labelling scheme. The carbonyl group occupies 25% of each α-position of the nitrogen atoms. The ellipsoids enclose 50% of the electronic density. The hydrogen atoms have been omitted for clarity. Symmetry operator \$1 : -x, 2-y, 1-z. The small black point indicates the position of the crystallographic inversion center.

## Calculations

Preliminary calculations, performed on **9** using the Extended Hückel Theory (EHT)[S1] with the CACAO program (**C**omputer **A**ided **C**omposition of **A**tomic **O**rbitals),[S2] revealed that the size of the molecular cavity is suitable for the insertion of transition metals such as $Ag^+$ assisted by coordination of the C⋯C bonds of the bridging ligands (Fig. S3).

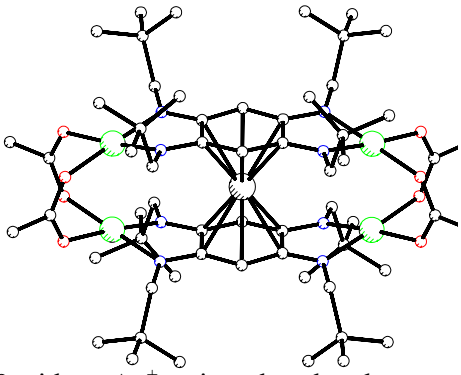

**Fig. S3** Calculated structure of **9** with an $Ag^+$ cation placed at the center of symmetry of the molecule.

## Crystal Structure Determinations

Diffraction data were collected on a Kappa CCD diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073 Å). The relevant data are summarized in Table 1. Data were collected using phi-scans and the structures were solved by direct methods using the SHELX 97 software,[S3,S4] and the refinement was by full-matrix least squares on $F^2$. No absorption correction was used. All non-hydrogen atoms were refined anisotropically with H atoms introduced as fixed contributors ($d_{C\text{-}H}$ = 0.95 Å, $U_{ll}$ = 0.04). Full data collection parameters, and structural data are available as Supporting Information. Crystallographic data for have been Crystallographic data for **9** and **11** have been deposited with the Cambridge Crystallographic Data Centre, CCDC 279434 and 619233, respectively.

## References

S1 (a) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.* 1962, **36**, 2179. (b) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.* 1963, **37**, 2872. (c) R. Hoffmann, *J. Chem. Phys.* 1963, **39**, 1397.

S2 C. Mealli and D. M. Proserpio, *J. Chem. Educ.* 1990, **67**, 399.

S3 Kappa CCD Operation Manual, Nonius B. V., Delft, The Netherlands, 1997
S4 Sheldrick, G. M. SHELXL97, Program for the refinement of crystal structures. University of Gottingen. Germany, 1997.