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Canopied *trans*-chelating bis(*N*-heterocyclic carbene) ligand: synthesis, structure and catalysis†

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The terphspan scaffold was employed to support a bis(*N*-heterocyclic carbene) ligand (**1**) that provides a *m*-terphenyl canopy over one side of its metal complexes. Single-crystal X-ray diffraction studies on a silver complex of $\{[Ag(\mathbf{1})]AgBr_2\}_2$ revealed an unusual tetranuclear silver core with a Ag–Ag bond distance of 3.0241(8) Å with **1** as a *trans*-chelating ligand (C–Ag–C = 171°). A preliminary X-ray structure of pseudo-square planar $[PdCl_2(\mathbf{1})]$ showed a similar binding mode of **1** (C–Pd–C = 177°). High yields were obtained in Suzuki–Miyaura coupling reactions utilizing $[PdCl_2(\mathbf{1})]$ as the procatalyst and the results were compared with analogous complexes of *trans*-spanning diphosphine (**2**) and diphosphinite (**3**) complexes. The diphosphinite complex, $[PdCl_2(\mathbf{3})]$, decomposes to $[\mu\text{-}ClPd(PPh_2OH)(PPh_2O)]_2$ at room temperature.

Introduction

The development of *N*-heterocyclic carbene (NHC) complexes in the 1960's[1,2] was followed by eventual isolation and crystallographic characterization of a stable, metal-free NHC by Arduengo *et al.* in 1991.[3] The unexpected stability and advantageous electronic properties of NHCs lead to an extensive investigation into their utility in synthesis, as ligands for transition metal complexes and in homogeneous catalysis.[4–8] Sterically encumbered NHCs have been particularly beneficial as ligands in next-generation catalysts with improved performance and thermal stability for olefin metathesis.[9–13] The ability of certain NHCs to dimerize, sometimes reversibly, has been exploited for the construction of new classes of π-conjugated materials for optoelectronic applications and self-healing polymers.[14–19] More recently, Robinson *et al.* has pioneered the application of sterically encumbered carbenes to stabilize reactive functionalities such as an Si=Si bond.[20]

Like phosphines, NHCs are good σ-donor ligands and they have consequently been explored as supporting ligands in catalytic transformations in which phosphines have long proven their value. One of the recent thrusts in phosphine-supported catalysis has been to affect selectivity by controlling the phosphine bite angle (P–M–P angle, β).[21–24] Specifically, there is an ongoing interest in wide bite angle (β greater than ~110°) or *trans*-spanning diphosphine ligands, which can provide superior regioselectivity in industrially important catalytic processes, notably rhodium catalyzed hydroformylation.[25–27] Because chelating bis(NHC)s have only been studied for the past two decades and the first chiral chelating NHC complex was not reported until 2000,[28] corresponding studies on bite angle dependence of NHC-supported catalysis remain in their early stages of development. This point is highlighted by the small number of bidentate bis(NHC)s whose transition metal complexes exhibit crystallographically characterized *trans*-chelating binding modes, representative examples of which are shown in Chart 1 (CSD version 5.29 Nov. 2007).[29–33]

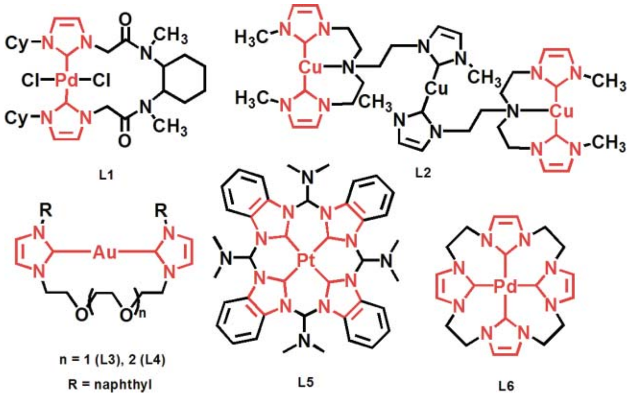

Chart 1 Examples of crystallographically characterized bidentate bis(NHC) complexes with C–M–C angles of ≥170°.

Previously, wide bite angle diphosphines built on the flexible terphspan scaffold have shown good activity for use in Pd-catalyzed Suzuki–Miyaura and Mizoroki–Heck couplings[34] and Rh-catalyzed 1,4-addition reactions of arylboronic acids to α,β-unsaturated ketones.[35] Protasiewicz *et al.* has further utilized C–X bond activation of terphspan diphosphines, diphosphinites and bis(imines) to yield cyclometallated C_2-symmetric terpincer ligands that are good candidates for asymmetric catalysis.[36–38] These promising initial data points suggest that the terphspan scaffold could be a worthy target for preparation of bis(NHC) complexes.

Herein, we describe a *trans*-chelating bis(NHC) built on the terphspan scaffold and compare its utility as a supporting ligand with that of terphspan diphosphine and diphosphinite ligands in Pd-catalyzed C–C bond formation *via* Suzuki–Miyaura coupling.

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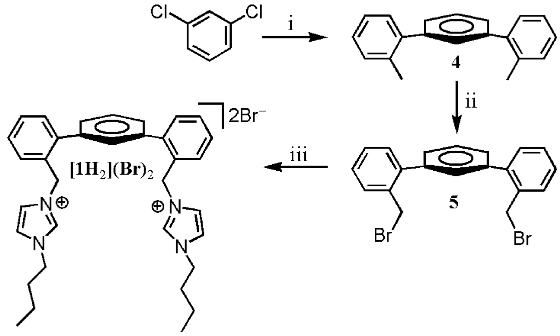
Results and discussion

Synthesis and reactivity

The preparation of the diphosphine **2** and diphosphinite **3** used in this study was carried out by modification of the literature reports.[39,40] The NHC complexes were prepared from the easily accessible bis(imidazolium) salt $[1H_2](Br)_2$ *via* the sequence shown in Scheme 1. The precursor $[1H_2](Br)_2$ is a viscous, hygroscopic oil melting near room temperature, and is difficult to obtain in a pure (>95%) form. The sample used for subsequent preparations was obtained by precipitation of the material as a white powder upon addition of a saturated dichloromethane solution into ethyl ether at −40 °C under a dry atmosphere followed by cold filtration and found to be pure (≥95%) by NMR spectroscopy (^{1}H and ^{13}C NMR spectra are provided in the ESI†).



Scheme 1 Preparation of $[1H_2](Br)_2$: (i) (1) ^{n}BuLi, −78 °C, THF, (2) 2-tolymagnesium bromide, −78 °C, THF, 6h, (3) Δ, 12 h (4) HCl, 0 °C; (ii) *N*-bromosuccinimide/benzoylperoxide, $CHCl_3$, Δ, 48 h; (iii) *N*-(*n*-butyl)imidazole, CH_3CN, Δ,12 h.

It was of interest to determine whether the free carbene ligand **1** could be generated or if the two carbene fragments would dimerize to form a tetraazafulvalene, as can sometimes occur for NHCs, a tendency that may be enhanced by the scaffold structure in bis(NHC)s.[41,42] The reaction of $[1H_2](Br)_2$ with 2 equiv. of NaH in anhydrous DMSO-d_6 at room temperature under a nitrogen atmosphere was thus undertaken and monitored by ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR resonance at 9.07 ppm, attributed to the protons in the imidazolium 2 position, rapidly disappeared from the ^{1}H NMR spectrum and a new resonance at 210.9 ppm was observed in the ^{13}C NMR spectrum. The latter peak is comparable to that observed in the initial report by Arduengo *et al.* on an isolable NHC (211.4 ppm in C_6D_6),[3] and was attributed to the free carbene unit in **1**. Unfortunately, X-ray quality crystals of free **1** have not been obtainable thus far. Although the depiction in Chart 2 suggests that bis(NHC) **1** may be predisposed to intramolecular dimerization, molecular modeling (semi-empirical PM3 level) revealed that dimerization would place significant strain on the scaffold and would require distortion of the central aryl ring of the *m*-terphenyl unit. The other possibility would be intermolecular dimerization to produce a polymer. However, we did not observe any increase in viscosity of reaction solutions even at very high concentrations (as high as 100 mg mL^{-1}) or evidence from NMR spectroscopy for polymerization, *i.e.*, broadening of resonances and disruption of molecular symmetry.

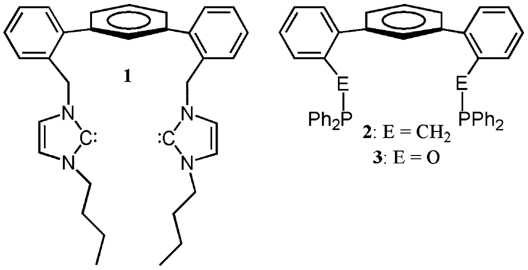


Chart 2 Structures of canopied ligands that chelate metals *via* carbene (**1**), phosphine (**2**) and diphosphinite (**3**) moieties.

The $[1H_2](Br)_2$ salt was employed to prepare the Ag(I) complex $[Ag(\mathbf{1})]AgBr_2$, (isolated as the dimer $\{[Ag(\mathbf{1})]AgBr_2\}_2$ shown in Fig. 1 in the solid state, *vide infra*) with the aim of using it as a convenient precursor to other complexes *via* transmetallation. $[Ag(\mathbf{1})]AgBr_2$ was readily prepared from $[1H_2](Br)_2$ and Ag_2O following a modified literature procedure for conversion of imidazolium salts to silver carbene complexes.[43] Analytically pure, but hygroscopic and light-sensitive, crystals of $[Ag(\mathbf{1})]AgBr_2$ (Fig. 1) were obtained either by slow diffusion of pentane into a saturated methylene chloride solution, or by slow evaporation of a saturated solution in acetone. Complete assignment of ^{1}H and ^{13}C NMR resonances for $[Ag(\mathbf{1})]AgBr_2$ were determined through a variety of NMR spectrometric techniques including ^{1}H–^{1}H correlation spectroscopy (COSY), heteronuclear multiple quantum coherence (HMQC), distortionless enhancement by polarization transfer (DEPT) and differential nuclear Overhauser effect (NOE). The original spectra from all of these techniques and the structural assignments derived from them are provided in the ESI.†

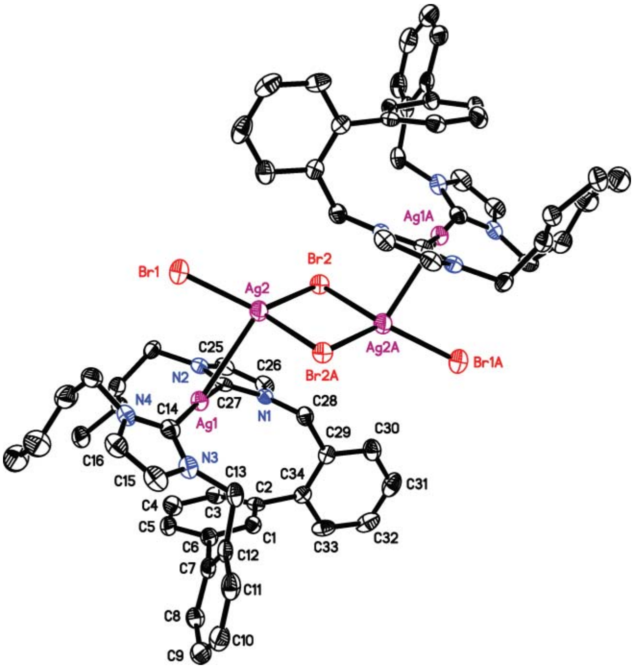


Fig. 1 ORTEP drawing (50% probability ellipsoids) of the molecular structure of $\{[Ag(\mathbf{1})]AgBr_2\}_2$. Hydrogen atoms are omitted for clarity.

The complex $[Ag(\mathbf{1})]AgBr_2$ was useful for the preparation of catalytically interesting late transition metal complexes by transmetallation. For example, $[Ag(\mathbf{1})]AgBr_2$ was cleanly converted to [PdCl$_2$(**1**)] by transmetallation with [PdCl$_2$(NCPh)$_2$] in dichloromethane at room temperature, and crystalline [PdCl$_2$(**1**)]·PhCH$_3$ was obtained by diffusion of toluene into a saturated solution in chlorobenzene. Whereas the phosphine analogue [PdCl$_2$(**2**)] shows broad and solvent dependent ^{1}H NMR resonances resulting from structural fluxionality, [PdCl$_2$(**1**)] shows sharp, well-resolved resonances. Even in ^{1}H and ^{13}C NMR spectra of the crystalline material, small side peaks are visible on some of the resonances attributable to atoms nearest the metal coordination site. This was initially thought to be indicative of two isomers that could possibly interconvert through different conformations of the 14-membered ring that includes the Pd atom, analogous to what was reported for [PdCl$_2$(**2**)].[40] The nature of these two isomers was elucidated by single-crystal X-ray diffraction studies, which identified the minor isomer as arising from variable occupancy of Br for some Cl on Pd (*vide infra*). Unfortunately, the two isomers could not be separated by preparative TLC or crystallization methods, and the material was therefore utilized as a mixture of isomers without separation. The ^{13}C NMR signal attributed to the carbene carbon (in CDCl$_3$), observed at 168.9 ppm, is comparable to the chemical shift observed in other *trans*-[PdCl$_2$(bis(NHC))] complexes (165.6–171.7 ppm).[44–46]

Structure

A single-crystal X-ray diffraction structure of {[Ag(**1**)]AgBr$_2$}$_2$ provided a structure (Fig. 1) in which a type 2 (Chart 3) binding mode is observed with a AgAg-μ-Br$_2$AgAg core being observed. Selected bond angles and distances listed in Table 1, and refinement details are provided in Table 2. The salient features are a Ag(1)–Ag(2) distance of 3.024 Å indicative of Ag–Ag bonding, and a cross-core Ag–Ag distance of 3.504 Å, which is not within the sum of the van der Waals radii (3.44 Å).[47] The unusual bis-μ-Br tetrametallic core of {[Ag(**1**)]AgBr$_2$}$_2$ (type 2 in Chart 3) has been observed only infrequently in Ag(I) NHC complexes previously,[48–54] and {[Ag(**1**)]AgBr$_2$}$_2$ appears to be the first example of a crystallographically characterized chelating NHC complex adopting this mode in the solid state.

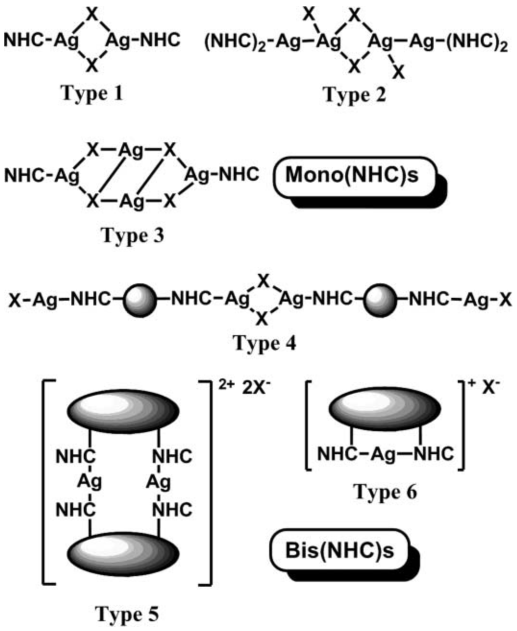


Chart 3 Some binding modes of silver(I) complexes featuring mono- (top) and bis- (bottom) *N*-heterocyclic carbene ligands that have been observed in the solid-state by X-ray diffraction.

Table 1 Selected bond lengths (Å) and angles (°) for {[Ag(**1**)]AgBr$_2$}$_2$

Bond lengths/Å	
Ag(1)–Ag(2)	3.0241 (8)
Ag(2)–Br(1)	2.5486 (8)
Ag(2)–Br(2)	2.6965 (11)
Ag(2)–Br(2)A[a]	2.7231 (8)
Ag(1)–C(14)	2.100 (5)
Ag(1)–C(27)	2.104 (5)
Bond angles/°	
C(27)–Ag(1)–C(14)	171.16 (18)
C(27)–Ag(1)–Ag(2)	62.88 (12)
C(14)–Ag(1)–Ag(2)	125.84 (13)
Br(1)–Ag(2)–Br(2)	129.40 (3)
Br(1)–Ag(2)–Br(2)A[a]	122.82 (3)
Br(2)–Ag(2)–Br(2)A[a]	99.45 (2)
Br(1)–Ag(2)–Ag(1)	80.86 (3)
Br(2)–Ag(2)–Ag(1)	134.14 (2)
Br(2)A[a]–Ag(2)–Ag(1)	84.37 (2)
Ag(2)–Br(2)–Ag(2)A[a]	80.55 (2)

[a] Symmetry transformations used to generate equivalent atoms: $-x + 1, -y + 1, -z$.

In one case of a complex exhibiting a type 2 binding mode (Chart 3), Lin, *et al.* aptly noted that the binding geometry can depend on the crystallization conditions, suggesting that different coordination modes may be operative in solution *vs.* the solid state.[48] Specifically, recrystallization of the type 2 crystals in the presence of a potentially coordinating solvent such as acetone allowed isolation of a type 1 binding mode (Chart 3). Following their lead, we collected structures of crystals grown either by diffusion of pentane into a CH$_2$Cl$_2$ solution of the silver complex or by slow evaporation of acetone. However, we observed the same binding mode from both types of crystals (the data from crystals grown in acetone refined better and yielded the data in Fig. 1 and Tables 1 and 2), indicating that this unusual binding motif is likely enforced by the scaffold.

On the basis of previous X-ray diffraction studies on Ag(I)-NHC complexes, we considered the possibility that one of the alternative binding modes shown in Chart 3 may be present in solution. Of these possibilities, type 1 and 3 binding modes require too far a separation between carbene fragments to be accommodated by a single **1** unit (as gauged by simple modelling using molecular mechanics), and are inconsistent with NMR data. The other binding modes may all be accommodated by the flexible terphenyl scaffold. Type 4 binding is ruled out by NMR spectrometry, which suggests a symmetry plane through the central aryl ring of the *m*-terphenyl unit. Type 5 binding, in which one carbene fragment from each unit of **1** binds to each of the two Ag(I) ions, cannot be ruled out on the basis of NMR data. This mode also seems plausible in light of a related structure that is formed for a dipalladium complex of Terphspan diphosphine **2**.[40] However, in diphosphine complexes utilizing the same scaffold, including [RhCl(CO)(**2**)] and [MCl$_2$(**2**)] (M = Ni, Pd, or Pt), as well as in

Table 2 Crystal data and structure refinement details

	$\{[Ag(\mathbf{1})]AgBr_2\}_2$	$[\mu\text{-}ClPd(PPh_2OH)(PPh_2O)]_2$	$[PdX_2(\mathbf{1})]\cdot PhCH_3$
Molecular formula	$C_{68}H_{76}Ag_4Br_4N_8$	$C_{48}H_{42}Cl_2O_4P_4Pd_2$	$C_{34}H_{38}Cl_{1.43}Br_{0.57}N_4Pd\cdots C_7H_8$
Formula weight/g mol^{-1}	1756.49	1090.40	797.46
Temperature/K	153 (2)	153 (2)	153(2)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$ (#14)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)
a/Å	15.262(3)	11.855(2)	10.392(2)
b/Å	10.348(2)	13.167(3)	13.675(3)
c/Å	21.561(4)	17.352(4)	15.092(3)
α/°	90.00	68.76(3)	109.66(3)
β/°	103.32(3)	78.84(3)	91.31(3)
γ/°	90.00	63.27(3)	111.21(3)
V/Å^3	3316.2(12)	2253.2(8)	1857.2(6)
Z	2	2	2
D_c/Mg m^{-3}	1.759	1.607	1.426
μ/mm^{-1}	3.620	1.103	1.250
F(000)	1736	1096	940
Crystal size/mm	0.46 × 0.22 × 0.12	0.53 × 0.48 × 0.36	0.22 × 0.17 × 0.10
Crystal colour and shape	Colourless chip	Yellow prism	Colourless chip
θ range for data collection/°	2.74–25.10	3.15–25.10	2.43–25.10
Limiting indices	$-18 < h < 18$ $-12 < k < 12$ $-25 < l < 25$	$-14 < h < 14$ $-15 < k < 14$ $-20 < l < 18$	$-10 < h < 12$ $-16 < k < 14$ $-18 < l < 18$
Reflections collected	21 729	16 023	13 822
Independent reflections	5901	7784	6539
Completeness to θ	25.10 (99.2%)	25.10 (97.0%)	25.10 (98.8%)
Max. transmission	0.6504	0.6923	0.8852
Min. transmission	0.2781	0.5926	0.7705
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5901/0/381	7784/0/567	6539/6/473
Goodness of fit on F^2	1.013	1.004	1.024
Final R indices ($I > 2\sigma(I)$)			
R_1	0.0389	0.0375	0.0583
wR_2	0.0732	0.0715	0.1073
R indices (all data)			
R_1	0.0465	0.0436	0.0922
wR_2	0.0779	0.0759	0.1196

$[PdCl_2(\mathbf{1})]$ (*vide infra*), the ligand adopts a *trans*-spanning mode such as that observed in the crystal structure for $\{[Ag(\mathbf{1})]AgBr_2\}_2$. Furthermore, due to the chelate effect it is entropically unlikely that the ligand-bridged type 5 core would form in the presence of coordinating bromide anions unless argentophilic interactions are strong enough to provide the necessary stabilization. The type 6 core is the most likely species to be present in solution on the basis of NMR and X-ray diffraction data. This species maintains the ligand-preferred *trans*-spanning mode and it can be easily envisioned that the type 2 core would be formed upon concentration of the solution without gross reorganization of the core.

The diffusion of toluene into a saturated solution of putative $[PdCl_2(\mathbf{1})]$ in chlorobenzene gave a preliminary structure of a bis-NHC palladium carbene with a *trans* chelating structure (Fig. 2). X-Ray diffraction analysis of one of these colourless crystals revealed that the halogen sites are both partially occupied by Br in addition to the expected Cl (Fig 2: X(1) = 61.63% Cl, 38.37% Br and X(2) = 81.18% Cl, 18.82% Br). Erker has reported observing similar mixed halogen occupation in a $[PdCl_2(NHC)]$ complex prepared by the same method we used to prepare $[PdCl_2(\mathbf{1})]$.[46] The partial occupancy in the current structure can be most easily denoted from the bond distances and angles listed in Table 3. Specifically, Pd–X(1) (2.377 Å) and Pd–X(2) (2.347 Å) interatomic distances are longer than the standard Pd–Cl bond (2.31 Å), which can be attributed to the larger van der Waals radius of bromide. The amount of bromide in X1 is more prominent as seen in the larger of the two bond distances (location of the X1 is in the less sterically hindered side). The C(14)–Pd(1)–C(25) angle of 176.8° is quite similar to the P–Pd–P angle observed in the terphspan phosphine complex $[PdCl_2(\mathbf{2})]$ 172.97°.[40]

NMR spectroscopic data also revealed important differences in the structural aspects of the terphspan carbene (**1**) and phosphine (**2**) complexes. Whereas the phosphine analogue $[PdCl_2(\mathbf{2})]$ shows broad and solvent-dependent ^{1}H NMR resonances resulting from structural fluxionality,[40] $[PdCl_2(\mathbf{1})]$ shows sharp, well-resolved resonances in both ^{1}H and ^{13}C NMR spectra. Another difference between the spectra of the phosphine complex $[PdCl_2(\mathbf{2})]$ and

Table 3 Selected bond lengths (Å) and angles (°) for $[PdX_2(\mathbf{1})]$

Bond lengths/Å	
Pd(1)–C(16)	2.015 (6)
Pd(1)–C(25)	2.031 (5)
Pd(1)–X(1)	2.3768 (15)
Pd(1) X(2)	2.3470 (16)
N(1)–C(16)	1.343 (8)
N(2)–C(16)	1.360 (8)
N(3)–C(25)	1.353 (7)
N(4)–C(25)	1.343 (7)

Bond angles/°	
C(16)–Pd(1)–C(25)	176.8 (3)
X(1)–Pd(1)–X(2)	175.75(6)
C(16)–Pd(1)–X(1)	90.69(18)
C(25)–Pd(1)–X(1)	90.26(17)
C(16)–Pd(1)–X(2)	88.08 (18)
C(25)–Pd(1)–X(2)	91.19 (17)
N(1)–C(16)–N(2)	105.3(5)
N(3)–C(25)–N(4)	105.2(4)

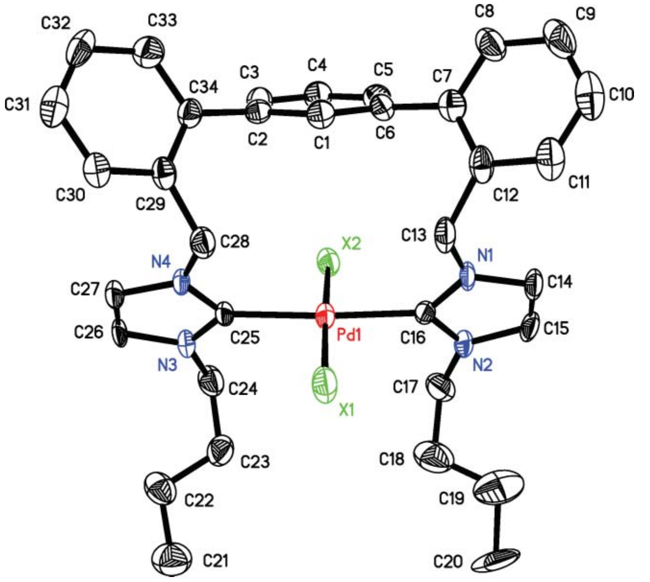


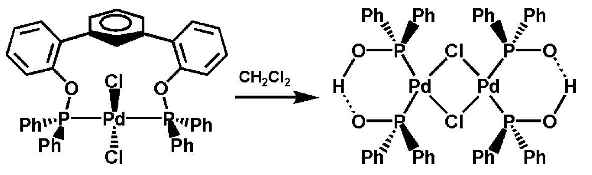
Fig. 2 ORTEP drawing (50% probability ellipsoids) of the molecular structure of $[X_2Pd(\mathbf{1})]$. Hydrogen atoms and the co-crystallized toluene solvent are omitted for clarity. C18, C19 and C20 show only one of the representative examples of the butyl partial occupancy observed. X1 = 61.63% Cl, 38.37% Br and X2 = 81.18% Cl, 18.82% Br.

the carbene complex $[PdCl_2(\mathbf{1})]$ are the positions of resonances attributable to H atoms on the central *m*-terphenyl ring. In $[PdCl_2(\mathbf{2})]$, these resonances are distributed over a broad range from 5.96–8.02 ppm due to interaction between the Pd–Cl and the aryl ring. However, in $[PdCl_2(\mathbf{1})]$, the larger Pd-containing ring size (14-atom *vs.* 12-atom in $[PdCl_2(\mathbf{2})]$) apparently positions the metal center too far from the central ring to engage in this type of interaction, with closest solid state Pd–Cl···H_{aryl} distances of 3.69 and 3.48 Å for $[PdCl_2(\mathbf{1})]$ and $[PdCl_2(\mathbf{2})]$, respectively, in the solid state.

Suzuki coupling: comparison of terphspan bis(NHC), diphosphine and diphosphinite

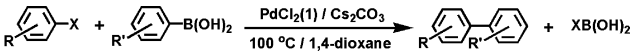
The canopied terphspan diphosphine **2** produces moderately active catalysts for Pd-catalyzed Suzuki–Miyaura coupling.[34] However, chelating NHC Pd complexes have produced a wide range of yields, from poor to excellent for this coupling reaction[44,55–68] and thus Suzuki–Miyaura coupling was the first reaction examined with terphspan carbene **1**. Because the coupling partners reported for reactions supported by **2** were rather limited in scope ($PhB(OH)_2$ was the only boronic acid employed), we expanded the set to include electron rich and electron deficient boronic acids as well as a heteroatom-containing aryl halide (2-iodothiophene) to gauge the compatibility of these species with reaction conditions (Table 3). That $[PdCl_2(\mathbf{1})]$ supports high yields employing 2-iodothiophene illustrates the use of heteroatom-containing aryl halides as successful reagents for coupling reactions. It is also noteworthy that **1** exhibits high yields in all cases (≥81%) when phenyl boronic acid is a coupling partner, while both electron donating (4-methoxyphenylboronic acid) and withdrawing (4-acetylphenylboronic acid) group substituted boronic acids sacrifice some efficiency, though modest yields are still achievable. The 4-acetylphenylboronic acid has substantially lower yields than reactions employing phenylboronic acid or 4-methoxyphenylboronic acid. Good to excellent yields are achievable utilizing a variety of aryl halides including aryl chlorides, bromides and iodides. This represents an improvement over coupling reactions employing diphosphine **2** under identical conditions, in which the highest yields achievable for coupling aryl chlorides and phenylboronic acid was 5%.[34] Modest to good yields (28–81%) were also observed utilizing $[PdCl_2(\mathbf{1})]$ for sterically encumbered aryl halides, such as 2,4,6-trimethylbromobenzene.

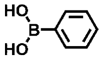
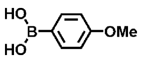
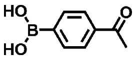
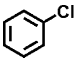
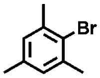
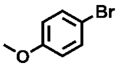
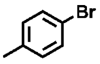
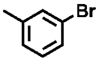
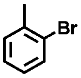
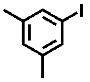
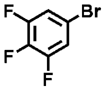
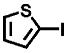
Having demonstrated that complexes of **1** can participate in efficient catalytic reactions, it was of interest to compare the relative efficiency of canopied carbene (**1**), diphosphine (**2**) and diphosphinite (**3**) ligands under identical reaction conditions. We therefore selected a subset of the reactions listed in Table 4 for testing with each of the three ligands (Table 5). As anticipated, catalytic reactions employing the diphosphinite ligand were generally much less efficient than analogous bis(NHC)- and diphosphine-supported reactions. Depressed yields of reactions employing the diphosphinite may be due to Pd-mediated decomposition of the ligand to species, such as $[ClPd(\mu\text{-}Cl)(PPh_2OH)]_2$ or $[\mu\text{-}ClPd(PPh_2OH)(PPh_2O)]_2$, though such species have also been employed in Stille–Miyaura coupling,[69–73] and related diphosphinite hydrolysis products have proven active in a variety of catalytic processes.[74–76] To determine whether ligand decomposition could be occurring in the current case, a solution of $[PdCl_2(NCPh)_2]$ and **3** in a 1 : 2 ratio was allowed to stand at room temperature under nitrogen in the absence of other reagents (Scheme 2).



Scheme 2 Decomposition of $[Cl_2Pd(\mathbf{3})]$ to form $[\mu\text{-}ClPd(PPh_2OH)(PPh_2O)]_2$.

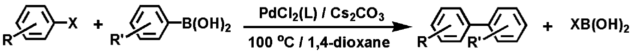
Table 4 Yields (GC-MS *vs.* internal calibration) of Suzuki–Miyaura coupling reactions in the presence of [Cl$_2$Pd(**1**)]



			
	96	83	99[b]
	81	52	28
	97	33	0
	82	90[a,b]	60
	90[a]	89[a,b]	8
	90[a]	96[a]	43
	~100	~100	65[a]
	~100	~100	57[a]
	95[a,b]	~100	39[a]

[a] Aryl halide homocoupling was observed. [b] A small amount of boronic acid self coupling was also observed.

Table 5 Yields of Suzuki–Miyaura coupling reactions in the presence of [Cl$_2$Pd(L)], where L = **1**, **2**, or **3**



ArB(OH)$_2$: Ar =	ArX	Ligand	Yield(%)
4-methoxyphenyl	PhCl	**1**	83
4-methoxyphenyl	PhCl	**2**	100
4-methoxyphenyl	PhCl	**3**	82
4-acetylphenyl	PhCl	**1**	99
4-acetylphenyl	PhCl	**2**	2
4-acetylphenyl	PhCl	**3**	2
Ph	2-bromotoluene	**1**	90
Ph	2-bromotoluene	**2**	100
Ph	2-bromotoluene	**3**	100

Crystals of [μ-ClPd(PPh$_2$OH)(PPh$_2$O)]$_2$ were indeed isolated from this mixture after 18 h (Fig. 3 and Table 6), and the initial yellow colour attributable to the putative [PdCl$_2$(**3**)] complex slowly fades to colourless. As seen in Table 4, the data referring to 4-acetylphenylboronic acid has considerable differences in yields depending on ligand substrate. The NHC ligand **1** emerges

Table 6 Selected bond lengths (Å) and angles (°) for [μ-ClPd(PPh$_2$OH)(PPh$_2$O)]$_2$

Bond lengths/Å	
Pd(1)–P(1)	2.2578 (10)
Pd(1)–P(2)	2.2510 (12)
Pd(1)–Cl(1)	2.4198 (10)
Pd(1)–Cl(1)A[a]	2.4284 (12)
P(1)–O(1)	1.537 (3)
P(2)–O(2)	1.539 (3)
Pd(2)–P(3)	2.2410 (13)
Pd(2)–P(4)	2.2449 (11)
Pd(2)–Cl(2)	2.4251 (13)
Pd(2)–Cl(2)A[b]	2.4297 (10)
P(3)–O(3)	1.542 (3)
P(4)–O(4)	1.536 (3)
Bond angles/°	
P(1)–Pd(1)–P(2)	92.56 (4)
P(1)–Pd(1)–Cl(1)	171.87 (3)
P(1)–Pd(1)–Cl(1)A[a]	89.77 (4)
P(2)–Pd(1)–Cl(1)	93.85 (4)
P(2)–Pd(1)–Cl(1)A[a]	177.06 (3)
Cl(1)–Pd(1)–Cl(1)A[a]	83.99 (4)
Pd(1)–Cl(1)–Pd(1)A[a]	96.01 (4)
P(3)–Pd(2)–P(4)	91.69 (5)
P(3)–Pd(2)–Cl(2)	168.14 (4)
P(3)–Pd(2)–Cl(2)A[b]	91.09 (4)
P(4)–Pd(2)–Cl(2)	93.84 (4)
P(4)–Pd(2)–Cl(2)A[b]	175.05 (3)
Cl(2)–Pd(2)–Cl(2)A[b]	84.19 (4)
Pd(2)–Cl(2)–Pd(2)A[b]	95.81 (4)

Symmetry transformations used to generate equivalent atoms: [a] $-x, -y + 1, -z + 1$. [b] $-x, -y + 2, -z + 2$.

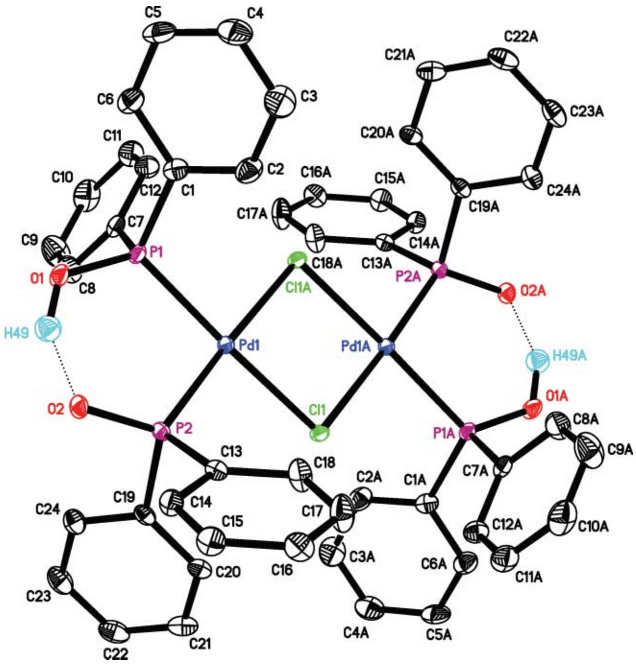


Fig. 3 ORTEP drawing (50% probability ellipsoids) of the molecular structure of [μ-ClPd(PPh$_2$OH)(PPh$_2$O)]$_2$. Hydrogen atoms are omitted for clarity however, H49 and H49A are shown to demonstrate hydrogen bonding.

as an obvious choice for coupling due to the advantageous yields achieved. It is also noteworthy that while diphosphine **2** provides poor (<5%) yields for coupling of aryl chlorides with either phenylboronic acid or 4-acetylphenylboronic acid, near quantitative coupling is achieved when 4-methoxyphenylboronic acid is employed. The generally good yields observed for all ligands used in this study for the coupling of phenylboronic acid with aryl bromides and iodides are also noteworthy.

Conclusions

We have prepared and characterized a *trans*-chelating bis(NHC) silver complex {[Ag(**1**)]AgBr$_2$}$_2$ that exhibits a unique tetranuclear core in the solid state. The synthesis of [PdCl$_2$(**1**)] was acheived *via* transmetallation and was shown to exhibit similar binding as [PdCl$_2$(**2**)]. The catalytic activity of canopied *trans*-chelating bis(NHC) ligands along with phosphine and diphosphinite analouges were explored for catalytic activity of C–C bond formation reactions *via* Suzuki–Miyaura coupling. Moderate to high yields and distinct differences in catalytic activity highlight the influence of *trans*-chelating complexes in catalytic processes. Additional studies on catalytic applications of wide bite angle bis(NHC) ligands are important ongoing efforts.

Experimental

General considerations

All air sensitive procedures were carried out in an inert atmosphere of nitrogen using an MBraun dry box or with standard Schlenk techniques. Compounds **2**[40] **3**,[39] **4**[77] and **5**,[78] were prepared as reported previously. Solvents were purified by passage through alumina columns under a N$_2$ atmosphere employing an MBraun solvent purification system. All other reagents were used as received from Aldrich Chemical Company, Acros, TCI and Alfa Aesar. NMR spectra were collected using a Bruker Avance 300 instrument operating at 300 MHz for proton and 75.4 MHz for ^{13}C. Gas chromatographs and mass spectra were collected using a Shimadzu GCMS-QP2010 and analyzed using the GCMS solution software.

Preparation of [1H$_2$](Br)$_2$

A solution of 1,3-bis[2-(bromomethyl)phenyl]benzene (1.00 g, 2.40 mmol) and *N*-(*n*-butyl)imidazole (0.656 g, 5.28 mmol) in acetonitrile (200 mL) was refluxed for 15 h. Once cooled to room temperature, the solvent was removed under reduced pressure to give an oily residue. Further purification was affected by re-precipitation from a saturated DCM solution into ethyl ether at −40 °C followed by cold filtration. The resulting solid was then dried *in vacuo* to yield a white powder that was used without further purification (1.46 g, 91.6%). ^{1}H NMR (300 MHz, DMSO-d$_6$) δ/ppm: 9.07 (s, 2H), 7.81 (s, 2H), 7.63–7.44 (m, 7H), 7.44–7.33 (m, 4H), 7.33–7.24 (m, 2H), 7.21 (s, 1H), 5.50 (s, 4H), 4.12 (t, 9.0 Hz, 4H), 1.69 (quintet, 6.0 Hz, 4H), 1.19 (sextet, 6.0 Hz, 4H), 0.85 (t, 7.5 Hz, 6H). ^{13}C{H} NMR (CD$_3$CN, 75.4 MHz) δ/ppm: 12.6, 18.9, 31.5, 49.4, 51.3, 122.4, 122.5, 128.1, 128.7, 128.8, 129.1, 129.6, 130.0, 130.8, 130.9, 135.3, 140.1, 141.7.

Preparation of [Ag(1)] AgBr$_2$

To a solution of 0.556 g (0.837 mmol) [1H$_2$](Br)$_2$ in 25 mL dichloromethane 0.239 g (1.03 mmol) silver(I) oxide was added. The suspension was refluxed for 24 h in the absence of light. The resulting solution was filtered through Celite and the filtrate was concentrated under reduced pressure then vacuum dried for 3 h to afford the product as a white powder. A minimal amount of DCM was used to dissolve the material and pentane was diffused into the vial at 0 °C to afford the pure complex as clear colourless crystals (0.632 g, 86.0%). High quality crystals for single-crystal X-ray diffraction were also attainable by slow evaporation of acetone. ^{1}H NMR (300 MHz, DMSO-d$_6$) δ/ppm: 7.75 (dd, 6.0 Hz, 2H), 7.48 (t, 7.5 Hz, 2H), 7.47 (d, 3.0 Hz, 2H), 7.43 (t, 7.5 Hz, 2H), 7.38 (t, 9 Hz, 1H), 7.38 (d, 3.0 Hz, 2H), 7.34 (bs, 1H), 7.21 (dd, 6.0 Hz, 2H), 6.95 (dd, 6.0 Hz, 2H), 5.43 (s, 4H), 3.96 (t, 7.5 Hz, 4H), 1.66 (quintet, 6.0 Hz, 4H), 1.20 (sextet, 9.0 Hz, 4H), 0.87 (t, 7.5 Hz, 6H). ^{13}C{H} NMR (75.4 MHz, DMSO-d$_6$) δ/ppm: 179.8, 142.2, 140.8, 134.1, 131.2, 131.2, 129.6, 129.1, 129.1, 128.6, 128.6, 122.8, 121.5, 53.1, 51.0, 33.6, 19.6, 13.9. Elemental analysis calcd for $C_{68}H_{76}Ag_4Br_2N_8 \cdot C_4H_8O$: (fw = 1662.13) C 47.29, H 4.63, N 6.13. Found: C 47.77, H 4.28, N 6.31.

Preparation of [PdCl$_2$(1)]

To a vigorously stirring solution of 0.0646 g (0.168 mmol) bis(benzonitrile) palladium(II) chloride (10 mm in dichloromethane) a 10 mm solution of 0.1493 g (0.157 mmol) [Ag(**1**)]AgBr$_2$ in dichloromethane was added dropwise. This solution was allowed to stir overnight then filtered and the filtrate was concentrated *in vacuo* then washed with hexane to afford a light yellow powder (0.0863 g, 80.9%) that was used immediately for coupling reactions. ^{1}H NMR (300 MHz, CDCl$_3$) δ/ppm: 7.63–7.30 (m, 10H) (dd, 6.0 Hz, 2H), 7.24 (dd, 7.7 Hz, 2H), 6.86 (d, 1.8 Hz, 2H), 6.76 (d, 2.1 Hz, 2H), 6.11 (s, 4H), 4.42 (t, 7.5 Hz, 4H), 2.03 (quintet, 7.5 Hz, 4H), 1.45 (sextet, 7.8 Hz, 4H), 1.00 (t, 7.2 Hz, 6H). ^{13}C{H} NMR (75.4 MHz, CDCl$_3$) δ/ppm: 168.9, 143.5, 140.1, 132.6, 132.4, 131.6 (131.7), 131.0, 130.8, 130.2, 128.5, 128.4, 120.8 (120.9), 119.1 (119.2), 52.4 (52.8), 50.4 (50.6), 33.4 (33.2), 20.1, 13.8. (peaks attributable to minor isomers are provided in parentheses; see ESI for original NMR spectra).† ESI-MS: *m*/*z* 689, (100%) [BrPd(**1**)]$^+$; *m*/*z* 645 (73.3%) [ClPd(**1**)]$^+$; *m*/*z* 608 (49.5%) [Pd(**1**)]$^+$.

General conditions for Suzuki coupling reactions

Conditions were identical to those reported for Suzuki coupling reactions utilizing ligand **2**.[34] A 5 mL vial equipped with a spin vain was charged with the requisite aryl halide (0.30 mmol), phenylboronic acid (0.45 mmol), Cs$_2$CO$_3$ (0.90 mmol), and 1 mol% of [PdCl$_2$(**1**)]. The components were then taken up in 2 mL 1,4-dioxane and heated at 100 °C under nitrogen for 25 h. Following the reaction, the crude reaction mixtures were diluted with diethyl ether for direct GC-MS analysis.

X-Ray crystallography

Intensity data were collected using a Rigaku Mercury CCD detector and an AFC8S diffractometer. Data collection and cell refinements were achieved using CrystalClear.[79] Data reduction and absorbance corrections were attained using REQAB.[80] The structures were solved by direct methods and subsequent Fourier difference techniques, and refined anisotropically, by full-matrix least squares, on F^2 using SHELXTL 6.10[81] All molecular graphics were generated using SHELXTL 6.10. Hydrogen atom positions were calculated from ideal geometry with coordinates riding on the parent atom however H49 and H50 in $[\mu\text{-ClPd(PPh}_2\text{OH)(PPh}_2\text{O)]}_2$ were located in the Fourier difference map, then refined. Partial occupancy was used to account for disorder observed in C47 and C48 of a phenyl ring in this structure. Disorder was observed in $[PdX_2(\mathbf{1})]\cdot C_7H_8$ on one of the ^{n}butyl functionalities and accounted for using partial occupancies of C18, C19 and C20 with their counterparts being C18A, C19A and C20A, respectively. The disorder in the co-crystallized toluene molecule in $[PdX_2(\mathbf{1})]\cdot C_7H_8$ was accounted for using partial occupancy of C41 with its counterpart being C41A.

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