The stabilization and reactivity of strained cyclic alkynes on transition metal centres

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Abstract - Small cycloalkynes that are short-lived or unknown in the free state can be stabilized by coordination to low-valent transition metal fragments such as ML_2 (M = Ni, Pt; L = various tertiary phosphines) or $ZrCp_2(PMe_3)$.[*] The preparation and reactivity of some of the resulting compounds, including $Pt(PPh_3)_2(cyclopentyne)$, $ZrCp_2(benzyne)(PMe_3)$, $ML_2(benzyne)$ (M = Ni, Pt; L = PEt_3, PPr_3^i, PCy_3), and $Ni_2(Cy_2PCH_2CH_2PCy_2)_2(\mu-1,4-benzdiyne)$, are discussed.

INTRODUCTION

A recurring theme in the development of organo-transition metal chemistry is the stabilization of highly reactive organic and inorganic fragments on a transition metal centre. An outstanding example is the short-lived, anti-aromatic hydrocarbon cyclobutadiene, the iron tricarbonyl complex of which is so stable that it undergoes typical aromatic substitution reactions. If required, free cyclobutadiene can be generated from this complex by treating it with oxidizing agents such as ceric ion (ref 1). Other molecules that can be stabilized by coordination to metal centres include carbenes, carbynes, phosphaalkynes and P_6. In most cases the short-lived fragment is not generated in the free state and trapped by the metal complex, but is generated on the metal centre from coordinated precursors.

The fact that most of the d-block elements from stable alkyne complexes suggests that it should be possible to stabilize small ring acetylenes by complexation. The smallest unsubstituted carbocyclic alkyne that can be isolated in the free state is cyclooctyne. Its smaller homologues cycloheptyne, cyclohexyne and cyclopentyne exist as transient, highly reactive molecules that oligomerize rapidly, although they can be trapped with reactive dienes (ref. 2-4). Probably the most well-known member of this class is benzyne (1,2-didehydrobenzene), formed by the removal of two adjacent substituents on a benzene ring (ref. 2,5,6). Benzyne is an intermediate in many aromatic substitution reactions of halogenobenzenes, but because it reacts readily with nucleophiles, it cannot be trapped with a reactive diene such as 2,5-diphenylisobenzofuran in these experiments unless a poorly nucleophilic base such as LiTMP is employed (eq 1) (ref. 7). Benzyne can also be generated by other methods including the reduction of o-dihalogenoarenes and the thermal decomposition of zwitterions such as benzenediazonium-2-carboxylate, and can be trapped by addition of reactive dienes (ref. 2,5,6). Similar methods are used for generating cycloalkynes (ref. 2-4).

(1)

METAL COMPLEXES OF SMALL CYCLOALKYNES

Stable platinum(0) complexes of cycloheptyne and cyclohexyne $Pt(PPh_3)_2(C_7H_{10})$ (**1**) and $Pt(PPh_3)_2(C_6H_8)$ (**2**), are obtained by reduction of the appropriate 1,2-dibromocycloalkenes with 1% sodium amalgam in the presence of $Pt(PPh_3)_3$ (ref. 8) (eq. 2).

n = 5 (**1**)   n = 4   (**2**)

(2)

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[*] Abbreviations: Cp = η^5-C_5H_5; Cp* = η^5-C_5Me_5; LiTMP = lithium 2,2,6,6-tetramethylpiperidide, $Li^+(C_5H_6Me_4N)^-$; Cy = cyclohexyl, C_6H_{11}; dppe = 1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$

We have also isolated the cyclohexyne complexes $PtL_2(C_6H_8)$ (L = PBu^tPh_2, PBu^t_2Ph) by a similar reaction in which $Pt(PPh_3)_3$ is replaced by the two-coordinate complexes PtL_2 (ref 9). The original idea behind these experiments was that the action of 1% sodium amalgam on the 1,2-dibromocycloalkenes would generate the free cycloalkyne, and that this would be trapped by the Pt(0) complex. An obvious alternative is that the 1,2-dibromocycloalkene oxidatively adds to the Pt(0) complex and that the resulting adduct is reduced by 1% sodium amalgam to give the cycloalkyne complex. Attempts to prepare the cyclopentyne or benzyne analogues of 1 and 2 by procedures similar to those of eq 2, starting from 1,2-dibromocyclopentene or dibromobenzene respectively, were unsucessful.

Recently we have found that 1,2-dibromocyclohexene oxidatively adds to $Pt(PPh_3)_2(C_2H_4)$ at room temperature to give cis-PtBr(C_6H_8Br)(PPh_3)$_2$ (3), and that this isomerizes to the corresponding trans-compound 4 in refluxing xylene (Fig. 1)(ref. 10). Neither 3 nor 4 is reduced by 1% sodium amalgam to 2, so these compounds cannot be intermediates in the formation of 2.
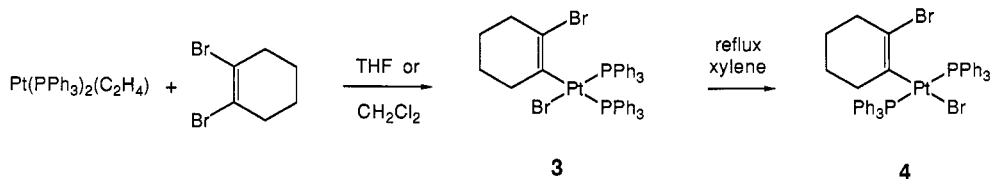
Fig. 1.   Oxidative addition of 1,2-dibromocyclohexene to $Pt(PPh_3)_2(C_2H_4)$

1,2-Dibromocyclopentene also reacts with $Pt(PPh_3)_2(C_2H_4)$ at room temperature, but in this case the first isolable product is the colourless, crystalline olefin complex $Pt(PPh_3)_2(\eta^2-C_5H_6Br_2)$ (5), the structure of which has been confirmed by X-ray crystallography (ref. 11) Migration of bromine from carbon to platinum occurs slowly in dichloromethane to give the cis-oxidative addition product, cis-PtBr(C_5H_6Br)(PPh_3)$_2$ (6), and this isomerizes in refluxing xylene to the trans-compound 7 (Fig. 2). As in the six-membered ring series, neither of the oxidative addition products is affected by 1% sodium amalgam. In contrast, the olefin complex 5 is reduced cleanly by 1% sodium amalgam to
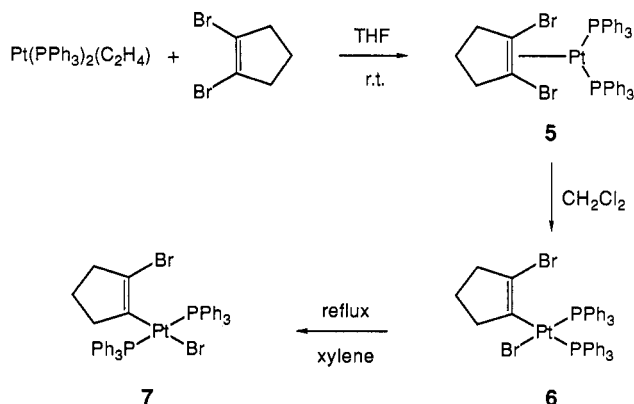
Fig. 2.   Reaction of 1,2-dibromocyclopentene with $Pt(PPh_3)_2(C_2H_4)$

give a colourless, very reactive solid that we formulate as the cyclopentyne complex $Pt(PPh_3)_2(C_5H_6)$ (8) (eq. 3) This observation suggests that the seven and six-membered ring analogues of 8, $Pt(PPh_3)_2$(1,2-dibromocycloheptene) and $Pt(PPh_3)_2$ (1,2-dibromocyclohexene) respectively, may be the key intermediates in the preparation of 1 and 2 in eq. 2, although they have never been detected.
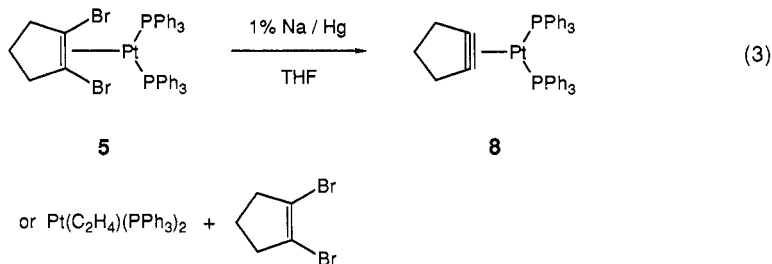
TABLE 1. Comparison of NMR data for $Pt(PPh_3)_2$(cycloalkyne)

$Pt(PPh_3)_2$(cycloalkyne)	C_7H_{10} (**1**)	C_6H_8 (**2**)	C_5H_6 (**8**)
$\delta_p(J_{PtP})$	29.4(3420)	28.3(3406)	28.0(3437)
δ(alkyne C)(J_{PtC})[a]	124.0(318)	131.6(395)	155.5(436)

[a] appears as a 5-line AA'X pattern owing to coupling with ^{31}P

Whereas the ^{31}P chemical shifts and Pt-P coupling constants for the cycloalkyne complexes **1**, **2** and **8** remain almost constant, the alkyne ^{13}C chemical shifts and Pt-C coupling constants increase with decreasing ring size (Table 1). If we assume that J_{PtC} correlates with the 6s-character of the bonding orbital used by platinum, the trend is consistent with the expected increase in metallacyclopropene character in the platinum-cycloalkyne interaction as the ring becomes smaller.

The infrared spectroscopic data are in agreement with this conclusion. The '$\upsilon(C\equiv C)$' frequency of **8** is remarkably low (1623 cm^{-1}) and suggests that the coordinated $C\equiv C$ distance in **8** may be very close to that of a double bond. The corresponding $C\equiv C$ distances in **1** and **2** (1.29 Å) are clearly longer than those in unstrained alkynes (1.21 Å) but are shorter than those in olefins (1.33 Å), and qualitatively this is reflected in the $\upsilon(C\equiv C)$ values for these complexes (1700-1800 cm^{-1}). A rough measure of the perturbation of the alkyne on coordination is provided by $\Delta\upsilon(C\equiv C)$, the difference between the $C\equiv C$ frequencies of the free and coordinated alkynes. The $\upsilon(C\equiv C)$ value of cycloheptyne has been measured in an argon matrix (ref. 12), but those of the smaller cycloalkynes are not known experimentally; they have, however, been estimated from ab-initio calculations (ref. 13). As shown in Table 2, $\Delta\upsilon(C\equiv C)$ decreases with decreasing ring size, perhaps indicating that the smaller cycloalkynes undergo less distortion on coordination than do the larger cycloalkynes.

TABLE 2. Comparison of IR data for cycloalkynes & their $Pt(PPh_3)_2$ complexes

	C_7H_{10}	C_6H_8	C_5H_6
$\upsilon(C\equiv C)$ (Complex)	1770(**1**)	1721(**2**)	1623(**8**)
$\upsilon(C\equiv C)$ (free ligand, singlet state)	2121	2003	1828
$\Delta\upsilon$	351	282	205

As expected, the $Pt(PPh_3)_2$(cycloalkyne) complexes become increasingly reactive as the ring becomes smaller. Cyclohexyne complexes such as $Pt(PPh_3)_2(C_6H_8)$ and $Pt(dppe)(C_6H_8)$ are readily protonated even by weak acids such as water or methanol to give η^1-cyclohexenylplatinum(II) complexes (ref. 8, 14)(eq. 4). The cyclopentyne complex **8**
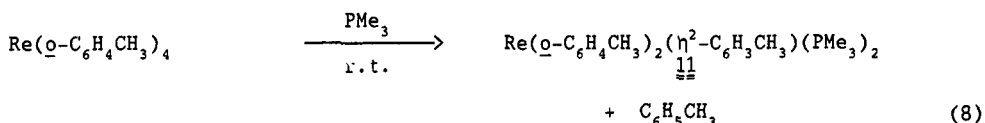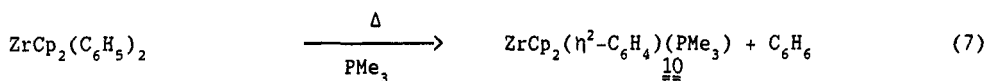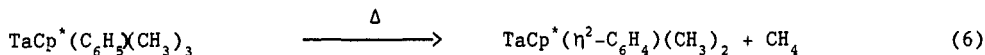

$$R = H, Me \tag{4}$$
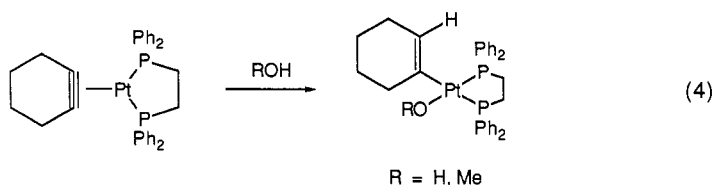
behaves quite differently. Instantaneously on treatment with methanol at room temperature, or more slowly in THF, it undergoes P-Ph bond cleavage of one of its PPh_3 ligands to give a dinuclear complex 9 which, as shown by X-ray crystallography, contains bridging PPh_2 and cyclopentene-1,2-diyl(μ-C_5H_6) groups (eq. 5) (ref. 11).

$$\tag{5}$$

8   9
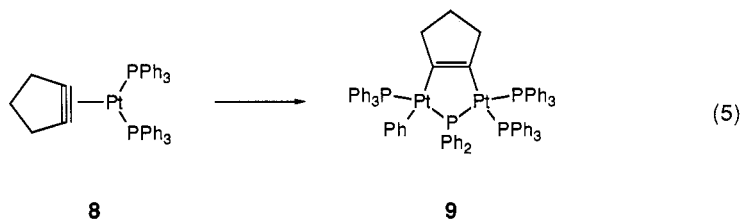
METAL COMPLEXES OF ARYNES

Aryne metal complexes are implicated as intermediates in the thermal decomposition of bis(aryl) or (aryl)(methyl) derivatives of the early transition elements and of uranium and thorium (ref. 15). The first structurally characterized mononuclear benzyne complex, $TaCp^*(C_6H_4)Me_2$, was made in this way (eq. 6) (ref. 16); subsequently aryne complexes of zirconium (**10**) (ref. 17) and rhenium (**11**) (ref. 18) (eq. 11,12), and bis(benzyne) complexes of niobium and tantalum (ref. 19), have been made similarly and structurally characterized.

$$TaCp^*(C_6H_5)(CH_3)_3 \xrightarrow{\Delta} TaCp^*(\eta^2\text{-}C_6H_4)(CH_3)_2 + CH_4 \qquad (6)$$

$$ZrCp_2(C_6H_5)_2 \xrightarrow[PMe_3]{\Delta} ZrCp_2(\eta^2\text{-}C_6H_4)(PMe_3) + C_6H_6 \qquad (7)$$
$$\underset{\mathbf{10}}{}$$

$$Re(\underline{o}\text{-}C_6H_4CH_3)_4 \xrightarrow[\text{r.t.}]{PMe_3} Re(\underline{o}\text{-}C_6H_4CH_3)_2(\eta^2\text{-}C_6H_3CH_3)(PMe_3)_2$$
$$\underset{\mathbf{11}}{}$$
$$+ \ C_6H_5CH_3 \qquad (8)$$

Unfortunately this method does not seem to be applicable to the later transition elements. The first mononuclear nickel(0)-benzyne complex $Ni(Cy_2PCH_2CH_2PCy_2)(C_6H_4)$, (**12**) was made by oxidative addition of o-dibromobenzene to the nickel(0)-ethylene complex, $Ni(Cy_2PCH_2CH_2PCy_2)(C_2H_4)$ (**13**), and reduction with 1% sodium amalgam of the resulting 2-bromophenylnickel(II) complex (Fig. 3) (ref. 20). We have extended this procedure to prepare the platinum analogue of **12** (ref. 21), and benzyne complexes of nickel(0) and platinum(0) containing monodentate trialkylphosphines, i.e. $ML_2(C_6H_4)$ (M = Ni, Pt; L = PCy_3, PPr^i_3, PEt_3) (ref. 22). In the case of platinum, 1% sodium amalgam is ineffective and it is necessary to use 43% sodium amalgam as the reducing agent. Analogous PMe_3 and PPh_3 complexes cannot be made in this way. Fortunately, the triisopropylphosphine ligands of $M(PPr^i_3)_2(C_6H_4)$ can be replaced completely or partly by other tertiary phosphines, so that a range of benzyne complexes containing tertiary phosphines of varying size and basicity is now available. The bis(triphenylphosphine) complexes $M(PPh_3)_2(C_6H_4)$, however, remain elusive.
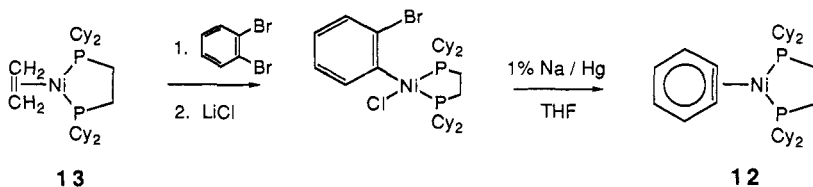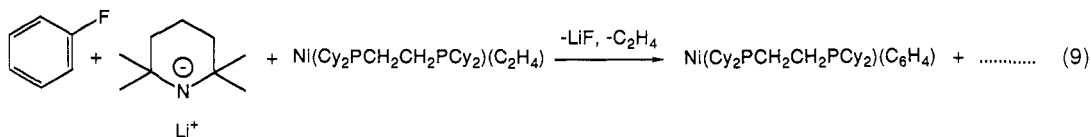

Fig. 3.   Preparation of $Ni(Cy_2PCH_2CH_2PCy_2)(C_6H_4)$ (**12**)

The nickel(0)-ethylene complex **13** behaves similarly to a reactive diene (eq 1) in its ability to trap free benzyne generated by the action of LiTMP on fluorobenzene (eq. 9). The ^{31}P NMR spectra show that benzyne complex **12** is formed in 15-20% yield, together with other unidentified products (ref. 23).

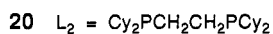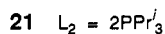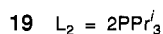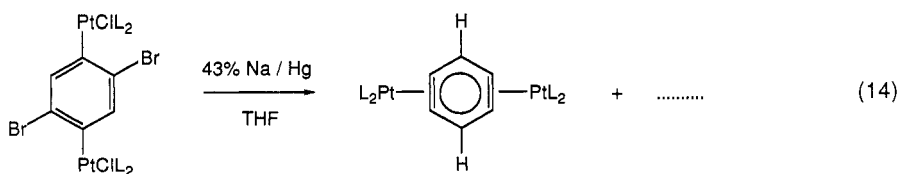Preliminary studies reveal marked differences in the reactivity of aryne complexes of different transition elements. The zirconium complex **10** acts as a source of the unsaturated fragment $ZrCp_2(C_6H_4)$, which readily undergoes insertion into the metal-benzyne bond with many multiply bonded molecules (e.g. alkenes, alkynes, ketones, nitriles) (ref. 17, 24). The nickel complex **12** similarly inserts methyl iodide, CO_2, ethylene, and dimethyl acetylenedicarboxylate (ref. 20). In contrast, the rhenium complex **11** is unaffected by most of these reagents (ref. 18). These differences are probably related to the ease with which a coordination site can be made available to the incoming molecules, and to steric effects.

The nickel- and platinum-benzyne complexes are very sensitive to protonic solvents. The nickel complexes react rapidly with primary and secondary alcohols to give alkoxides; these are unstable at room temperature and eliminate benzene with formation of a nickel(0) complex of the corresponding aldehyde or ketone (eq. 10)

$$(10)$$

$$(11)$$

$$+$$

$$CH_3CHO$$

The platinum (II) methoxide $Pt(OMe)(C_6H_5)(Cy_2PCH_2CH_2PCy_2)$ made from $Pt(Cy_2PCH_2CH_2PCy_2)(C_6H_4)$ and methanol is stable at room temperature, but is rapidly hydrolysed by water to the corresponding hydroxide. The platinum(II) alkoxides made from $PtL_2(C_6H_4)$ (L = PEt_3, PPr_3^i) decompose at room temperature, but in a different way from the nickel complexes. The products are trans-$PtH(C_6H_5)L_2$ and, presumably, the corresponding aldehyde or ketone (eq 11) (ref. 22).

METAL COMPLEXES OF BENZDIYNE

In view of the successes with cycloalkynes and benzyne, it is clear that transition elements should be able to stabilize even more strained small rings containing several triple bonds. Two examples are the isomers 1,3- and 1,4-benzdiyne, derived by removal of four substituents from a benzene ring (Fig. 4). These molecules are unknown in the free state, although synthetic equivalents have been generated by treatment of 1,2,3,4- and 1,2,4,5- tetrabromoarenes with two equivalents of an organolithium reagent (ref. 25).

Fig. 4. 1,3- and 1,4-Benzdiyne

Buchwald et al (ref. 26) have recently reported the formation of di-zirconium complexes of both isomers, 14 and 15, by thermal decomposition of the p-phenylene-zirconocene complex 16 in the presence of trimethylphosphine (eq. 12). The di-zirconium complex of 1,4-dimethoxy-1,4-benzdiyne (17) (eq. 13) has been structurally characterized.

$$(12)$$

16   **14**   **15**

$$(13)$$

This methodology cannot be used to make dinickel(0) or diplatinum(0) complexes. The ideal precursors to 1,4-benzdiyne complexes of these elements would seem to be 2,5- dibromobenzene-1,4-diyl metal complexes 18.

18

We have been unable to make such compounds by double oxidative addition of 1,2,4,5-tetrabromobenzene to nickel(0) and platinum(0) precursors. In the case of platinum, however, double oxidative addition of 2,5-dibromo-1,4-benzenedicarboxylic acid chloride to $Pt(PPh_3)_4$, and subsequent thermal elimination of CO and replacement of PPh_3, has given the desired precursors 19 and 20. These can be reduced by 43% sodium amalgam to give the first diplatinum(0) complexes of 1,4-benzdiyne 21 and 22 in yields of 10-30% (eq. 14).

$$(14)$$

19 $L_2 = 2PPr^i_3$ **21** $L_2 = 2PPr^i_3$

20 $L_2 = Cy_2PCH_2CH_2PCy_2$ **22** $L_2 = Cy_2PCH_2CH_2PCy_2$

$$(15)$$

23   **13**   **24**

In the case of nickel, a different approach has been used, which is based on the ability
of the nickel(0)-ethylene complex 13 to trap free benzyne (eq. 9). Treatment of the 4-
fluorobenzynenickel(0) complex 23 with a large excess of LiTMP in the presence of 13 gives
the first dinickel(0) complex of 1,4-benzdiyne (24) (eq. 15) (ref. 23). The yield of 24
is remarkably high (60-70%), which may imply that the likely intermediate,
$Ni(Cy_2PCH_2PCy_2)$(1,4-benzdiyne), fairly long-lived. The geometry and dimensions of 24 are
similar to those of the benzyne complex 12, the $C_6H_2Ni_2$ moiety being essentially planar;
the alkyne C-C distances are 1.313(12) Å, and the remaining C-C distances are in the range
1.40-1.42 Å.

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