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Homo-Diels–Alder Cycloadditions Catalysed by Cobalt–Triphenylphosphine–Zinc Systems

I-Farn Duan,[a] Chien-Hong Cheng,*[a] Juan-Su Shaw,[b] Sheng-San Cheng[b] and Kuo Fu Liou[b]

[a] *Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, Republic of China*
[b] *Chung-Shan Institute of Science and Technology, PO Box 90008-17, Lung-Tan, Taiwan, Republic of China*

$[CoI_2(PPh_3)_n]$–zinc systems (n = 1 or 2) exhibit high catalytic activity for the homo-Diels–Alder [2 + 2 + 2] cycloadditions of norbornadiene with various alkynes including terminal and internal acetylenes and methyl prop-2-ynyl ether to give the corresponding deltacyclenes in good to excellent yields.

Metal-catalysed homo-Diels–Alder [2 + 2 + 2] cycloadditions[1] have attracted considerable attention recently, finding potential application in multi-ring synthesis, in catalytic asymmetric induction[2] and in the synthesis of high energy fuels.[3] Following the initial discovery of the cobalt-catalysed cycloadditions of norbornadiene (NBD) with alkynes (Scheme 1) by Lyons *et al.*,[4] the catalyst systems have been limited to $[Co(acac)_3]$, Hacac = pentane-2,4-dione, bidentate phosphines and alkylaluminium chlorides. Lautens and Crudden[5] showed that the catalytic activity was greatly enhanced when $[Co(acac)_3]$ was azeotropically dried prior to being reduced, but cobalt systems appear to be effective only with terminal alkynes, reactions with internal alkynes being unsatisfactory. We are interested in highly strained multi-ring compounds as high energy fuels, and we now report a conveniently prepared new cobalt system which is not only more active than the previous catalysts but also readily catalyses the cycloaddition of internal alkynes with norbornadiene to give deltacyclic products.

This system consists of the monodentate phosphine complex $[CoI_2(PPh_3)_n]$ (n = 1 or 2)[6] and zinc powder. Typically, to a mixture of $[CoI_2(PPh_3)_2]$ (0.267 mmol) and zinc powder (2.67 mmol) in dichloromethane (6 ml) was added hex-1-yne (11.3 mmol) and norbornadiene (10.9 mmol). The solution was stirred at 20 °C for 20 min. Concentration followed by separation on a silica gel column gave the corresponding deltacyclic product **1**. Other terminal alkynes including phenylethyne, hept-1-yne and ethyne reacted similarly to give the corresponding deltacyclenes **2**, **3** and **4**, respectively, in excellent yields. The reaction of NBD with ethyne was very rapid and exothermic and the catalytic activity appeared to be retained throughout the reaction. This system also catalysed

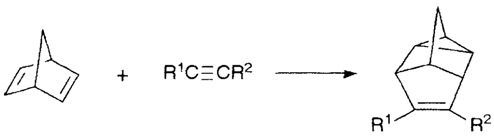

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Table 1 [2 + 2 + 2] Homo-Diels–Alder reactions between NBD and alkynes catalysed by cobalt complexes (Scheme 1)[a]

R^1	R^2	Catalyst	Solvent	t/h	θ/°C	Product	Yield (%)[c]
Bu^n	H	$CoI_2 + 2\,PPh_3$	CH_2Cl_2	0.33	19	**1**	93
Bu^n	H[b]	$[CoI_2(PPh_3)]$	CH_2Cl_2	0.50	28	**1**	96
Bu^n	H[b]	$[CoI_2(PPh_3)_2]$	CH_2Cl_2	0.50	28	**1**	50
Bu^n	H[b]	$[CoI_2(PPh_3)_2] + 2\,PPh_3$	CH_2Cl_2	0.50	28	**1**	20
Bu^n	H[b]	CoI_2 + dppe	CH_2Cl_2	0.50	28	**1**	Trace
Bu^n	H[b]	CoI_2 + dppe	CH_2Cl_2	5.5	28	**1**	78
Ph	H	$CoI_2 + 2\,PPh_3$	CH_2Cl_2	0.33	20	**2**	95
Et	Et	$CoI_2 + 2\,PPh_3$	CH_2ClCH_2Cl	1	81	**7**	87
Pr^n	Me	$[CoI_2(PPh_3)_2]$	CH_2ClCH_2Cl	2.5	64	**6**	84
Me_3Si	H[d]	$[CoI_2(PPh_3)_2]$	CH_2Cl_2	5	40	**5**	65
$Me[CH_2]_4$	H	$[CoI_2(PPh_3)_2]$	CH_2Cl_2	0.5	20	**3**	96
$MeOCH_2$	H	$[CoI_2(PPh_3)_2]$	CH_2ClCH_2Cl	72	56	**8**	46
H	H	$[CoI_2(PPh_3)_2]$	CH_2Cl_2	1.5	20	**4**	92

[a] Except where otherwise noted, molar ratio NBD : alkyne : cobalt : zinc = 40 : 40 : 1 : 10; 0.247 mmol of cobalt complex and 6 ml of solvent were employed for each run. [b] Molar ratio of NBD : alkyne : cobalt : zinc = 100 : 100 : 1 : 10. [c] Isolated yield based on NBD used. [d] Molar ratio NBD : trimethylsilylethyne : cobalt = 20 : 60 : 1. [e] Molar ratio NBD : ethyne : cobalt = 16 : 25 : 1.

the cycloaddition of trimethylsilylethyne with NBD to afford **5** in 65% yield. The results and conditions are in Table 1. It is noteworthy that the same catalytic activity was obtained if $[CoI_2(PPh_3)_n]$ was replaced by $CoI_2 + n\ PPh_3$.

As found by Lautens and Crudden,[5] the reaction is extremely sensitive to the solvent. The use of solvents such as benzene and tetrahydrofuran (THF)–benzene which were effective for reactions using $[Co(acac)_3]$–Et_2AlCl led to low yields of the desired products. Dichloromethane and 1,2-dichloroethane, in which $[CoI_2(PPh_3)_2]$ is highly soluble, are the two most efficient solvents. $[CoI_2(PPh_3)_2]$ is only slightly soluble in benzene or THF–benzene. Solvents with substantial coordinating ability such as THF, dimethylformamide and dimethyl sulphoxide also dissolve $[CoI_2(PPh_3)_n]$, but the homo-Diels–Alder reaction is not catalysed if they are used as solvents. Thus, it appears that solvents need to dissolve $[CoI_2(PPh_3)_n]$ readily, but also coordinate weakly to the metal centre.

The $[CoI_2(PPh_3)_2]$–Zn system also catalyses the [2 + 2 + 2] cycloadditions of NBD with internal alkynes including hex-2-yne, and hex-3-yne to give the corresponding deltacyclic products **6** and **7**, respectively, in excellent yields. These additions do take place at ambient temperature, but higher temperatures are required for reasonable rates. The cycloadditions of internal alkynes were thus better carried out in 1,2-dichloroethane instead of the low boiling-point dichloromethane. The same cobalt–zinc system is also active for the cycloaddition of methyl prop-2-ynyl ether with NBD to yield the corresponding deltacyclene **8**; the present system is the only effective catalyst for the cycloaddition of internal dialkylalkynes and methyl prop-2-ynyl ether with NBD.

$[CoI_2(PPh_3)_2]$ and $[CoI_2(PPh_3)]$ in the presence of zinc powder are both excellent catalyst systems for the [2 + 2 + 2] reactions, but to see which is best both were used in the reaction of NBD with hexy-1-yne under the same conditions. The reacting solutions were quenched after being stirred at room temperature for 20 min. The yields of the corresponding deltacyclene were 38 and 12%, respectively, indicating that $[Co(PPh_3)I_2]$ is more active than $[Co(PPh_3)_2I_2]$. Addition of free PPh_3 to these solutions further decreased the product yield. A plot of product yield *vs.* equiv. of PPh_3 gave a maximum at 1 equiv. of PPh_3. Replacement of $[CoI_2(PPh_3)_n]$ by CoI_2 led to no reaction between NBD and hex-1-yne. These observations lead us to conclude that there is only one PPh_3 attached to the cobalt centre in the active catalyst intermediate. Dissociation of one PPh_3 from $[CoI_2(PPh_3)_2]$ was involved in the rate-limiting steps of the observed catalysis. In agreement with these conclusions, when $[CoI_2(dppe)]$–zinc (dppe = 1,2-bisdiphenylphosphinoethane) was employed as the catalyst system for the same reaction, only a trace of the expected deltacyclene was observed. Although $[CoI_2(PPh_3)]$ is more active than $[CoI_2(PPh_3)_2]$, it is less stable, and sometimes decomposed gradually resulting in lower yields. In the absence of zinc powder, no catalytic reaction was observed suggesting that a low-oxidation-state cobalt complex is involved in the catalytic reaction. At ambient temperature the $[CoI_2(PPh_3)_2]$–zinc system in the absence of alkyne catalysed the dimerization of NBD in essentially quantitative yield. On the other hand, hex-1-yne was slowly trimerized to the corresponding benzene derivative by the same system in the absence of NBD. The dimerization of NBD[6,7] and trimerization of ethyne[8] catalysed by cobalt complexes have been reported. Although the exact nature of the catalyst intermediate is not known, these results as well as the observed high yields of deltacyclenes strongly indicate that the coordination of both NBD and alkyne are greatly favoured over the coordination of two NBD or two alkyne units to the same intermediate.

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References

1 G. N. Schrauzer and P. Glockner, *Chem. Ber.*, 1964, **97**, 2451; S. Yoshikawa, K. Aoki, J. Kiji and J. Furukawa, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 3239; S. Yoshikawa, J. Kiji and J. Furukawa, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 1093; M. Lautens and L. G. Edwards, *Tetrahedron Lett.*, 1989, **30**, 6813; M. Lautens and L. G. Edwards, *J. Org. Chem.*, 1991, **56**, 3761.

2 M. Lautens, J. C. Lautens and A. C. Smith, *J. Am. Chem. Soc.*, 1990, **112**, 5627; H. Brunner, M. Muschiol and F. Prester, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 652.

3 J. E. Lyons, W. A. Schneider, O. Hills, H. K. Myers and J. Aston, U.S. Pat., 1979, 4 132 742, H. K. Myers, J. Aston, J. E. Lyons, W. A. Schneider and O. Hills, U.S. Pat., 1978, 4 110 409.

4 J. E. Lyons, H. K. Myers and A. Schneider, *J. Chem. Soc., Chem. Commun.*, 1978, 636.

5 M. Lautens and C. M. Crudden, *Organometallics*, 1989, **8**, 2733.

6 G. N. Schrauzer, R. K. Y. Ho and G. Schlesinger, *Tetrahedron Lett.*, 1970, 543.

7 G. N. Schrauzer, B. N. Bastian and G. A. Fosselius, *J. Am. Chem. Soc.*, 1966, **88**, 4890.

8 K. P. C. Vollhardt, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 539; R. L. Hillard, III, C. A. Parnell and K. P. C. Vollhardt, *Tetrahedron*, 1983, **39**, 905; C. J. Saward and K. P. C. Vollhardt, *Tetrahedron Lett.*, 1975, 4539.