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Reaction of [M(η^3-allyl)(η^2-amidinato)(CO)$_2$(pyridine)] complexes (M = Mo, W) with bidentate ligands: nitrogen donor *vs.* phosphorus donor†

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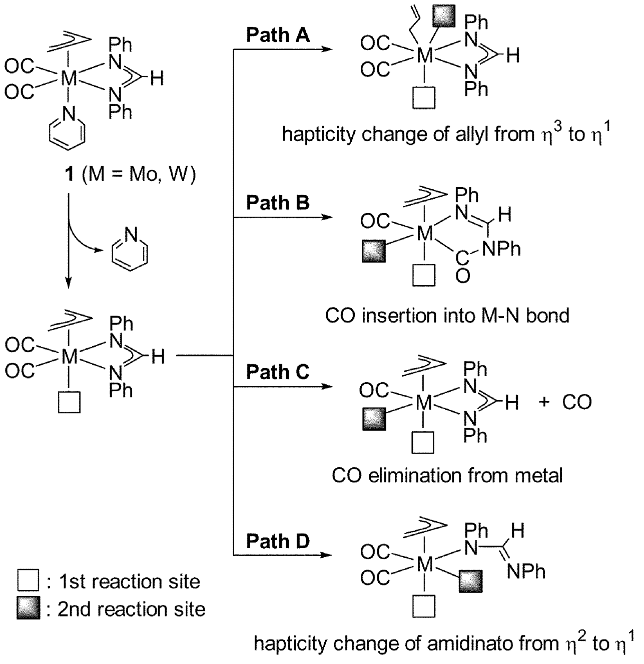
The reactivity of amidinato complexes of molybdenum and tungsten bearing pyridine as a labile ligand, [M(η^3-allyl)(η^2-amidinato)(CO)$_2$(pyridine)] (M = Mo; **1-Mo**, M = W; **1-W**), toward bidentate ligands such as 1,10-phenanthroline (phen) and 1,2-bis(diphenylphosphino)ethane (dppe) was investigated. The reaction of **1** with phen at ambient temperature resulted in the formation of monodentate amidinato complexes, [M(η^3-allyl)(η^1-amidinato)(CO)$_2$(η^2-phen)] (M = Mo; **2-Mo**, M = W; **2-W**), which has pseudo-octahedral geometry with the amidinato ligand coordinated to the metal in an η^1-fashion. The phen ligand was located coplanar with two CO ligands and the η^1-amidinato ligand was positioned *trans* to the η^3-allyl ligand. In solution, both complexes **2-Mo** and **2-W** showed fluxionality, and complex **2-Mo** afforded allylamidine (**3**) on heating in solution. In the reaction of **1** with dppe at ambient temperature, the simple substitution reaction took place to give dppe-bridged binuclear complexes [{M(η^3-allyl)(η^2-amidinato)(CO)$_2$}$_2$(μ-dppe)] (M = Mo; **5-Mo**, M = W; **5-W**), whereas mononuclear monocarbonyl complexes [M(η^3-allyl)(η^2-amidinato)(CO)(η^2-dppe)] (M = Mo; **6-Mo**, M = W; **6-W**) were obtained under acetonitrile- or toluene-refluxing conditions. Mononuclear complex **6** was also obtained by the reaction of binuclear complex **5** with 0.5 equivalents of dppe under refluxing in acetonitrile or in toluene. The X-ray analyses and variable-temperature ^{31}P NMR spectroscopy of complex **6** indicated the existence of the rotational isomers of the η^3-allyl ligand, *i.e.*, *endo* and *exo* forms, with respect to the carbonyl ligand. The different reactivity of complex **1** toward phen and dppe seems to have come from the difference in the π-acceptability of each bidentate ligand.

Introduction

η^3-Allyldicarbonyl complexes of molybdenum and tungsten often play an important role in both coordination chemistry[1] and catalytic organic transformations.[2] A series of allyl complexes of Mo and W have been prepared by the reaction of [M(η^3-allyl)X(CO)$_2$(NCMe)$_2$] (M = Mo, W; X = Cl, Br),[3] which is a good precursor for a coordinatively unsaturated reactive intermediate due to possessing two labile acetonitrile and one halide ligands, with four-electron donating neutral ligands[4] as well as anionic ligands.[5] Although an amidinato ligand, which acts as an anionic four-electron donor, has been known to be one of the most important heteroallylic ligands capable of controlling the stability and/or reactivity of metal complexes because of its ability to act as both chelating and bridging modes toward metals as reviewed by Kilner[6] and Edelmann,[7] there has been no investigation on this respect. We have started our research on the amidinato complexes of Mo and W, and have recently reported the preparation and some reactivity of amidinato complexes formulated as [M(η^3-allyl)(η^2-amidinato)(CO)$_2$(pyridine)] (M = Mo; **1-Mo**, M = W; **1-W**).[8a]

The complex **1** has one labile pyridine ligand, which is easily substituted by two-electron donor such as PR$_3$ to afford the corresponding phosphine-coordinated complex.[8] In our further studies on the reactivity of **1**, we were interested in its reaction with bidentate four-electron donor such as 1,10-phenanthroline (phen) and 1,2-bis(diphenylphosphino)ethane (dppe). Four possible reaction sites would be expected in the coordinatively unsaturated species formed by dissociation of the pyridine ligand as depicted in Scheme 1.[6] The first one accompanies the hapticity change of the allyl ligand from the η^3- to the η^1-mode, whose dynamic behavior has been demonstrated using nucleophilic solvent as a Lewis base (Path A).[9] The second one contains the insertion of one of the CO ligands into metal–amidinato nitrogen bond to give a carbamoyl-type complex



Scheme 1

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† Electronic supplementary information (ESI) available: ORTEP drawings of complexes **2**, **5** and **6** with the atom-numbering scheme and 2D-NMR spectra of complex **6**. See http://www.rsc.org/suppdata/dt/b4/b410927a/

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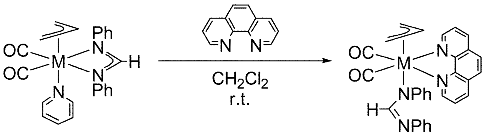
(Path B).[10] The dissociation of CO ligand is the third route (Path C). There is also a rare example in which the η^2-amidinato ligand converts into the η^1-amidinato ligand (Path D). We investigated the reactions of **1** with phen and dppe, and found differences of the reactivity of the amidinato complex **1** depending on these four-electron donor molecules.

Results and discussion

Reaction of amidinato(pyridine) complexes 1 with phen. Formation of η^1-amidinato complexes

On treatment of complex **1-Mo** with one equivalent of 1,10-phenanthroline (phen) in CH_2Cl_2 at room temperature, an initial yellow solution instantaneously changed to a red solution from which red crystals were isolated in 87% yield. In a case of tungsten complex **1-W**, a similar reaction took place to give red crystals in 85% isolated yield. Elemental analyses, IR, low-temperature ^{1}H NMR spectra, and X-ray diffraction studies established the formation of η^1-amidinato complex formulated as [M(η^3-allyl)(η^1-amidinato)$(CO)_2$(η^2-phen)] (M = Mo; **2-Mo**, M = W; **2-W**) (eqn. (1)).



1-Mo (M = Mo)
1-W (M = W)

2-Mo (M = Mo)
2-W (M = W)

(1)

In the IR spectra, both complexes showed two CO stretching bands at 1931 and 1842 cm^{-1} for **2-Mo**, and 1921 and 1828 cm^{-1} for **2-W**. These observations indicate that two carbonyl ligands are located in mutually *cis* positions. The ^{1}H NMR spectrum of **2-Mo** at ambient temperature showed broad signals, whereas sharp signals were observed at low temperature (at −40 °C). Allyl protons were observed at 1.47 (*anti*-CH_2), 2.72 (central proton) and 3.16 (*syn*-CH_2) ppm. Four sets of phenanthroline protons were detected at 7.65 (s), 7.79 (dd, J = 7.9, 4.6 Hz), 8.32 (dd, J = 7.9, 1.3 Hz), and 9.12 (dd, J = 4.6, 1.3 Hz) ppm with each of 2H integration. Similar spectroscopic data were obtained by low-temperature ^{1}H NMR measurement of **2-W**. These observations suggest the geometry of **2** possessing a mirror plane through the central carbon of the allyl group, M (Mo or W), and the coordinated nitrogen atom of the amidinato ligand. In order to confirm η^1-coordination mode of the amidinato ligand in complex **2**, X-ray diffraction analyses of complexes **2-Mo** and **2-W** were undertaken.

The ORTEP drawing of complex **2-Mo** is displayed in Fig. 1. Complex **2-W** showed similar structural features as **2-Mo**. The crystal data and selected bond distances and angles are listed in Tables 1–3, respectively. Complexes **2-Mo** and **2-W** have pseudo-octahedral geometry around the central metal, and have amidinato ligand coordinated to the metal with η^1-coordination mode. The phen ligand was located coplanar with two CO ligands, and the η^1-amidinato ligand positioned *trans* to the allyl ligand. The open face of the allyl ligand was directed toward two carbonyl ligands, which has been known to be a favorable orientation for a series of [M(η^3-allyl)$(CO)_2$] complexes (M = Mo, W).[11] The geometry of these complexes revealed by X-ray analyses coincides with the results obtained by low-temperature ^{1}H NMR measurements described above.

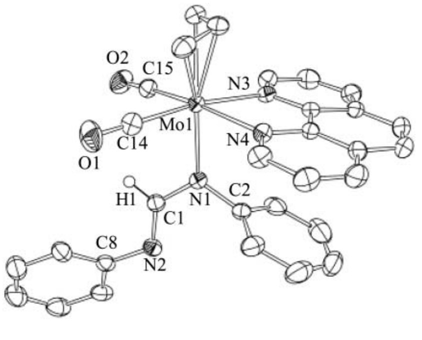


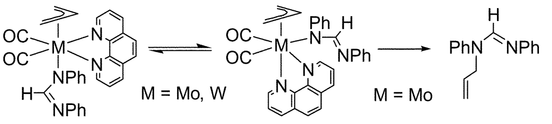
Fig. 1 ORTEP drawing of **2-Mo** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms except for H1 are omitted for clarity.

In the amidinato ligand in complex **2**, the N(1)–C(1) bond distances (1.353(4) Å for **2-Mo** and 1.356(5) Å for **2-W**) are slightly longer than the N(2)–C(1) bond distances (1.296(4) Å for **2-Mo** and 1.286(5) Å for **2-W**). However, these bond distances are within the mean value of the N–C single bond (1.48 Å) and the N–C double bond (1.24 Å),[6] indicating that the amidinato N–C–N bond electrons are delocalized even in η^1-coordination mode. The covalent Mo(1)–N(1) bond distance in **2-Mo** is 2.199(3) Å, which is slightly shorter than the dative Mo–N(amidine) bond distance in the amidinato(amidine) complex of molybdenum (2.25(2) Å for [Mo(η^3-allyl){η^2-$(NPh)_2CH$}$(CO)_2$(*N*,*N*′-diphenylformamidine)].[8b] Similar results have been reported in Pt[12] and Hg[13] complexes bearing η^1-amidinato or amidine ligands.

It has been reported that the M–N–Y–N (Y = CH or N) skeleton in the related compounds such as amidine,[12] amidinato,[12,13] or triazenido[14] shows the '*cisoid*' arrangement as a common feature. It was concluded that the '*cisoid*' conformation is electronically favored over the '*transoid*' one. In this respect, it is noteworthy that the M–N–C–N skeleton in the complexes **2-Mo** and **2-W** adopts the '*transoid*' arrangement. Furthermore, the '*transoid*' Mo–N–C–N skeleton was also found in the amidinato(amidine) complex of Mo mentioned above.[8b] The adaptation of the '*transoid*' conformation in our system seems to have come from the steric reason.

Complexes **2-Mo** and **2-W** in solution showed fluxional behavior as observed by ^{1}H NMR spectroscopy. As is already mentioned above, the low-temperature ^{1}H NMR spectrum suggested that the presence of a mirror plane consisting of the central allyl carbon, metal, and the amidinato nitrogen which is in agreement with the X-ray analyses. We next investigated the fluxional behavior of complexes **2-Mo** and **2-W** at higher temperatures, which was monitored by ^{1}H NMR in DMSO-d_6.

In the case of molybdenum complex **2-Mo**, the broad signals observed at room temperature did not change up to about 65 °C. On further raising the temperature the sharp signals being assignable to the new product appeared at 70 °C. In order to characterize the product, we examined this thermal reaction in a Schlenk tube and a pale yellow waxy solid was isolated from the reaction mixture. The characterization of the waxy solid was achieved spectroscopically to indicate the formation of allylamidine **3** in 53% yield (eqn. (2)). It is conceivable that the formation path of the allylamidine **3** from **2-Mo** is *via* intramolecular reductive elimination between the allyl and amidinato ligands. Recently, Pérez and co-workers have reported systematic studies on the reductive elimination of molybdenum complexes from a viewpoint of the Mo-catalyzed allylic alkylation.[15] Their results demonstrated that allylic alkylation (C–C bond formation) occurs *via* reductive elimination when the allyl and nucleophilic groups are in mutually *cis* positions. In the complex **2-Mo**, the allyl and η^1-amidinato ligands are found to be located in mutually *trans* positions in the solid state and in solution at low-temperature. The formation of an allylamidine at higher temperature suggests that the allyl and amidinato ligands can adopt mutually *cis* positions (***cis*-2** in eqn. (2)) by a fluxional process.



2   ***cis*-2**   **3**

(2)

Table 1 Summary of crystal data for complexes **2**, **5** and **6**

	2-Mo·CH_2Cl_2	**2-W**	**5-Mo**	**5-W**	**6-Mo**·$\frac{1}{2}$PhMe	**6-W**·$\frac{1}{2}$PhMe
Empirical formula	$C_{31}H_{26}Cl_2MoN_4O_2$	$C_{30}H_{24}N_4O_2W$	$C_{31}H_{28}MoN_2O_2P$	$C_{31}H_{28}N_2O_2PW$	$C_{46.5}H_{44}MoN_2OP_2$	$C_{46.5}H_{44}N_2OP_2W$
Formula weight	653.42	656.40	587.49	675.40	804.76	892.67
Crystal color, habit	Red, needle	Red, needle	Orange, plate	Orange, plate	Orange, needle	Orange, needle
Crystal size/mm	0.25 × 0.13 × 0.10	0.38 × 0.15 × 0.10	0.25 × 0.18 × 0.08	0.18 × 0.18 × 0.05	0.30 × 0.18 × 0.10	0.25 × 0.10 × 0.08
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
Lattice parameters						
a/Å	14.259(3)	12.735(3)	11.232(3)	11.208(3)	14.023(3)	14.011(3)
b/Å	9.974(3)	15.578(3)	11.608(3)	11.606(6)	14.404(4)	14.373(3)
c/Å	20.134(3)	14.442(3)	11.209(3)	11.186(2)	10.863(3)	10.874(3)
α/°			96.37(2)	96.21(2)	107.28(2)	107.36(2)
β/°	94.50(1)	115.59(2)	107.50(3)	107.41(1)	110.37(2)	110.27(2)
γ/°			71.83(2)	71.85(3)	74.54(2)	74.37(2)
V/Å^3	2854(1)	2583(1)	1324.1(7)	1319.2(8)	1931.2(9)	1926.5(9)
Z	4	4	2	2	2	2
D_c/g cm^{-3}	1.520	1.687	1.473	1.700	1.384	1.539
F_{000}	1328.00	1288.00	602.00	666.00	834.00	898.00
μ(Mo-Kα)/cm^{-1}	6.82	45.11	5.86	44.76	4.61	31.24
Reflections measured	9094	8111	8094	8056	11807	11770
Independent reflections (R_{int})	8327 (0.039)	7530 (0.054)	7729 (0.043)	7705 (0.028)	11254 (0.035)	11219 (0.033)
No. variables	465	431	418	418	607	607
Reflection/parameter ratio	17.91	17.47	18.49	18.43	18.54	18.48
Residuals: R; R_w	0.082; 0.123	0.054; 0.087	0.069; 0.108	0.047; 0.076	0.067; 0.111	0.051; 0.085
Residuals: $R1$	0.044	0.031	0.039	0.028	0.040	0.031
No. of reflections to calc $R1$	5204 ($I > 2.0\sigma(I)$)	5744 ($I > 2.0\sigma(I)$)	5954 ($I > 2.0\sigma(I)$)	6658 ($I > 2.0\sigma(I)$)	8517 ($I > 2.0\sigma(I)$)	9444 ($I > 2.0\sigma(I)$)
Goodness of fit Indicator	0.98	0.94	1.05	0.91	1.09	0.96
$\delta\rho_{max, min}$/e Å^{-3}	0.52, −0.57	1.48, −1.07	0.68, −0.59	0.70, −0.76	0.70, −0.59	0.79, −1.11

Table 2 Selected bond distances (Å) and angles (°) for molybdenum complexes **2-Mo**, **5-Mo** and **6-Mo**

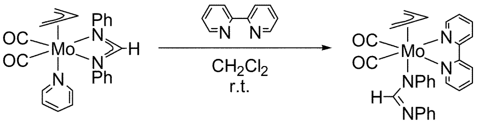
	2-Mo		**5-Mo**		**6-Mo**	
CO	Mo(1)–C(14)	1.960(4)	Mo(1)–C(14)	1.968(3)	Mo(1)–C(14)	1.898(3)
	Mo(1)–C(15)	1.966(4)	Mo(1)–C(15)	1.951(3)	O(1)–C(14)	1.180(3)
	O(1)–C(14)	1.158(4)	O(1)–C(14)	1.159(4)		
	O(2)–C(15)	1.156(4)	O(2)–C(15)	1.164(4)		
Amidinato	Mo(1)–N(1)	2.199(3)	Mo(1)–N(1)	2.229(2)	Mo(1)–N(1)	2.210(2)
	N(1)–C(1)	1.353(4)	Mo(1)–N(2)	2.272(2)	Mo(1)–N(2)	2.362(2)
	N(2)–C(1)	1.296(4)	N(1)–C(1)	1.332(3)	N(1)–C(1)	1.334(3)
			N(2)–C(1)	1.325(3)	N(2)–C(1)	1.312(3)
Others around M	Mo(1)–N(3)	2.242(3)	Mo(1)–P(1)	2.5677(7)	Mo(1)–P(1)	2.5460(8)
	Mo(1)–N(4)	2.252(3)			Mo(1)–P(2)	2.4427(6)
CO	Mo(1)–C(14)–O(1)	177.3(3)	Mo(1)–C(14)–O(1)	176.8(3)	Mo(1)–C(14)–O(1)	176.7(2)
	Mo(1)–C(15)–O(2)	177.1(3)	Mo(1)–C(15)–O(2)	177.5(3)		
Amidinato	Mo(1)–N(1)–C(1)	121.1(2)	Mo(1)–N(1)–C(1)	95.3(2)	Mo(1)–N(1)–C(1)	97.1(2)
	Mo(1)–N(1)–C(2)	123.3(2)	Mo(1)–N(1)–C(2)	139.9(2)	Mo(1)–N(1)–C(2)	139.8(2)
	C(1)–N(1)–C(2)	114.8(3)	C(1)–N(1)–C(2)	123.9(2)	C(1)–N(1)–C(2)	122.8(2)
	N(1)–C(1)–N(2)	126.6(3)	Mo(1)–N(2)–C(1)	93.6(2)	Mo(1)–N(2)–C(1)	90.8(2)
	C(1)–N(2)–C(8)	116.5(3)	Mo(1)–N(2)–C(8)	143.1(2)	Mo(1)–N(2)–C(8)	149.0(2)
			C(1)–N(2)–C(8)	123.1(2)	C(1)–N(2)–C(8)	120.2(2)
			N(1)–C(1)–N(2)	112.3(2)	N(1)–C(1)–N(2)	114.1(2)
Others around M	N(3)–Mo(1)–N(4)	73.34(10)	N(1)–Mo(1)–N(2)	58.69(8)	N(1)–Mo(1)–N(2)	57.97(7)
	N(3)–Mo(1)–C(15)	99.4(1)	N(1)–Mo(1)–C(15)	106.5(1)	N(1)–Mo(1)–C(14)	105.86(9)
	C(14)–Mo(1)–C(15)	81.3(1)	C(14)–Mo(1)–C(15)	79.6(1)	P(2)–Mo(1)–C(14)	81.65(8)
	C(14)–Mo(1)–N(4)	104.6(1)	C(14)–Mo(1)–N(2)	113.9(1)	P(2)–Mo(1)–N(2)	113.74(5)
					N(1)–Mo(1)–P(2)	154.39(6)
					N(2)–Mo(1)–C(14)	163.71(9)

Table 3 Selected bond distances (Å) and angles (°) for tungsten complexes **2-W**, **5-W** and **6-W**

	2-W		**5-W**		**6-W**	
CO	W(1)–C(14)	1.956(4)	W(1)–C(14)	1.958(4)	W(1)–C(14)	1.901(4)
	W(1)–C(15)	1.958(4)	W(1)–C(15)	1.968(4)	O(1)–C(14)	1.188(4)
	O(1)–C(14)	1.167(5)	O(1)–C(14)	1.157(5)		
	O(2)–C(15)	1.161(5)	O(2)–C(15)	1.162(5)		
Amidinato	W(1)–N(1)	2.173(3)	W(1)–N(1)	2.263(3)	W(1)–N(1)	2.202(3)
	N(1)–C(1)	1.356(5)	W(1)–N(2)	2.227(3)	W(1)–N(2)	2.342(3)
	N(2)–C(1)	1.286(5)	N(1)–C(1)	1.324(4)	N(1)–C(1)	1.333(5)
			N(2)–C(1)	1.332(4)	N(2)–C(1)	1.312(4)
Others around M	W(1)–N(3)	2.257(3)	W(1)–P(1)	2.5586(8)	W(1)–P(1)	2.538(1)
	W(1)–N(4)	2.238(3)			W(1)–P(2)	2.4381(8)
CO	W(1)–C(14)–O(1)	178.6(4)	W(1)–C(14)–O(1)	177.6(3)	W(1)–C(14)–O(1)	176.7(3)
	W(1)–C(15)–O(2)	176.5(4)	W(1)–C(15)–O(2)	177.5(4)		
Amidinato	W(1)–N(1)–C(1)	119.9(3)	W(1)–N(1)–C(1)	94.0(2)	W(1)–N(1)–C(1)	97.4(2)
	W(1)–N(1)–C(2)	124.5(3)	W(1)–N(1)–C(2)	142.6(2)	W(1)–N(1)–C(2)	139.3(2)
	C(1)–N(1)–C(2)	114.7(3)	C(1)–N(1)–C(2)	123.2(3)	C(1)–N(1)–C(2)	123.0(3)
	N(1)–C(1)–N(2)	126.8(4)	W(1)–N(2)–C(1)	95.4(2)	W(1)–N(2)–C(1)	91.7(2)
	C(1)–N(2)–C(8)	116.7(4)	W(1)–N(2)–C(8)	139.3(2)	W(1)–N(2)–C(8)	147.9(2)
			C(1)–N(2)–C(8)	124.6(3)	C(1)–N(2)–C(8)	120.5(3)
			N(1)–C(1)–N(2)	111.9(3)	N(1)–C(1)–N(2)	112.9(3)
Others around M	N(3)–W(1)–N(4)	73.2(1)	N(1)–W(1)–N(2)	58.7(1)	N(1)–W(1)–N(2)	57.9(1)
	N(3)–W(1)–C(15)	104.3(1)	N(1)–W(1)–C(15)	114.2(1)	N(1)–W(1)–C(14)	105.5(1)
	C(14)–W(1)–C(15)	80.3(2)	C(14)–W(1)–C(15)	79.5(2)	P(2)–W(1)–C(14)	81.7(1)
	C(14)–W(1)–N(4)	101.2(2)	C(14)–W(1)–N(2)	106.3(1)	P(2)–W(1)–N(2)	114.08(8)
					N(1)–W(1)–P(2)	154.37(8)
					N(2)–W(1)–C(14)	163.3(1)

It is reported that 16-electron square-planer late-transition metal complexes bearing the '*cisoid*' η^1-amidinato or triazenido ligand often show fluxional behavior. The most likely process in these complexes involves the intermediacy of a chelated *N*,*N*′-bonded amidinato or triazenido ligand.[12,14] In our system, which are of coordinatively saturated metal complexes involving '*transoid*' η^1-amidinato ligand, the twisted mechanism, which is generally accepted for a series of η^3-allyldicarbonyl complexes of molybdenum and tungsten,[16] seems to be conceivable for the explanation of the fluxional process.[17] In a case of tungsten complex **2-W**, on the other hand, no transformation of the complex was observed up to 85 °C in DMSO-d_6.

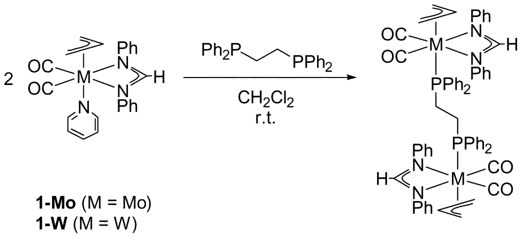
The reaction of **1-Mo** with 2,2′-bipyridine (bpy) occurred instantly to form a red solution. After work-up, a red powder was obtained and was analyzed by IR spectroscopy. The CO stretching bands were observed at 1928 and 1840 cm^{-1}, which are similar to those for the phen complex **2-Mo** (1931 and 1842 cm^{-1}), indicating the product being a bpy complex having an η^1-amidinato ligand (**4**), as is supported by elemental analysis (eqn. (3)). Furthermore, heating **1-Mo** in pyridine did not afford a monodentate bis(pyridine) complex containing η^1-amidinato ligand and the complex **1-Mo** remained intact. These results indicate that the bidentate nitrogen ligands such as phen and bpy play an important role to produce η^1-amidinato complexes.



1-Mo **4** (3)

Reaction of amidinato(pyridine) complexes 1 with dppe. Formation of μ-dppe binuclear and η^2-dppe mononuclear complexes

In the reaction of **1** with bidentate nitrogen compounds such as phen and bpy, it was found that the fourth reaction pattern (Path D) depicted in Scheme 1 proceeds and that the η^1-amidinato complex is formed. We next examined the reaction of **1** with the bidentate phosphorus ligand, 1,2-bis(diphenylphosphino)ethane (dppe). Upon treatment of molybdenum complex **1-Mo** with dppe in CH_2Cl_2 at ambient temperature, a homogeneous yellow solution gradually turned to a heterogeneous system and afforded an orange precipitate (**5-Mo**, 60% isolated yield). A similar feature was observed with tungsten complex **1-W**, *i.e.*, an orange precipitate was formed (**5-W**, 60% isolated yield) (eqn. (4)).



1-Mo (M = Mo)
1-W (M = W)

5-Mo (M = Mo)
5-W (M = W) (4)

In the IR spectra, two CO stretching bands at 1924 and 1843 cm^{-1} for **5-Mo** and at 1916 and 1831 cm^{-1} for **5-W** were observed, whose stretching bands were slightly higher than those for PEt_3 complexes of Mo[8b] and W,[8a] respectively. These observations indicate that the simple substitution reaction of the pyridine ligand by dppe occurred and that two carbonyl ligands were located in mutually *cis* positions. Complex **5** was so poorly soluble toward various organic solvents that the spectroscopic data could not be obtained satisfactorily. The X-ray analyses of these complexes revealed the formation of dppe-bridged binuclear complexes, [{M(η^3-allyl)(η^2-amidinato)$(CO)_2$}$_2$(μ-dppe)] (M = Mo; **5-Mo**, M = W; **5-W**).

Single crystals of **5-Mo** and **5-W** for X-ray analyses were directly obtained from the reaction mixture in CH_2Cl_2. The ORTEP drawing of complex **5-Mo** is displayed in Fig. 2. The crystal data and selected bond distances and angles are listed in Tables 1–3, respectively.

X-Ray analyses of complexes **5-Mo** and **5-W** revealed the dppe-bridged binuclear skeletons, which have pseudo-octahedral geometry around each metal. The amidinato ligand is located at an equatorial position and is coplanar with two CO ligands. The dppe phosphorus is at an axial position *trans* to the η^3-allyl ligand in both complexes. The metal–phosphorus bond distances are 2.5677(7) Å for **5-Mo** and 2.5586(8) Å for **5-W**, which are remarkably similar to those in the PEt_3 coordinated mononuclear complexes [M(η^3-allyl)(η^2-amidinato)$(CO)_2PEt_3$] (M = Mo, W).[8] Other geometrical features around the central metal are also similar to those for the mononuclear complexes bearing the PEt_3 ligand. Furthermore, the bond distances and angles in **5-Mo** have a close similarity to those of tungsten complex **5-W**.

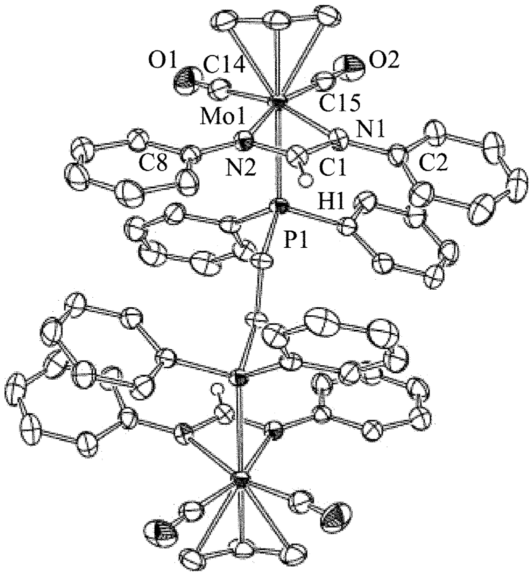
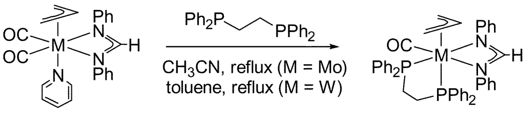


Fig. 2 ORTEP drawing of **5-Mo** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms except for H1 (and H1*) are omitted for clarity.

When the reactions between **1** and dppe were performed under refluxing conditions in acetonitrile for molybdenum or in toluene for tungsten, the mononuclear complexes formulated as [M(η^3-allyl)(η^2-amidinato)(CO)(η^2-dppe)] (M = Mo; **6-Mo**, M = W; **6-W**) were formed (eqn. (5)). The reaction of **1-Mo** with one equivalent of dppe in acetonitrile under reflux resulted in a homogeneous red solution, from which [Mo(η^3-allyl)(η^2-amidinato)(CO)(η^2-dppe)] (**6-Mo**) was isolated in 59% yield. The similar reaction with tungsten complex **1-W** afforded mononuclear complex **6-W** with concomitant formation of binuclear complex **5-W**. Complex **6-W** was obtained as a single component under toluene-refluxing conditions and isolated in 50% yield.



1-Mo (M = Mo)
1-W (M = W)

6-Mo (M = Mo)
6-W (M = W) (5)

The reaction of binuclear **5-Mo** with dppe under acetonitrile-refluxing conditions afforded complex **6-Mo** in 73% isolated yield, suggesting the stepwise reaction path in the reaction of **1** with dppe; binuclear complex **5** forms at the first stage and then converts to mononuclear complex **6**. The reaction of **5-W** with dppe under toluene-refluxing conditions also afforded complex **6-W** in 56% isolated yield.

X-Ray diffraction studies of complexes **6-Mo** and **6-W** were undertaken. The ORTEP drawing of complex **6-Mo** is displayed in Fig. 3. The crystal data and selected bond distances and angles are listed in Tables 1–3, respectively.

Complexes **6-Mo** and **6-W** are pseudo-octahedral mononuclear complexes having one CO and η^2-dppe ligands. The CO and one phosphorus are coplanar with the amidinato ligand, and the other phosphorus of dppe and η^3-allyl ligands are in mutually *trans* positions.

Compared with a series of dicarbonyl complexes **2** and **5**, the metal–carbonyl moiety in complex **6** shows slightly

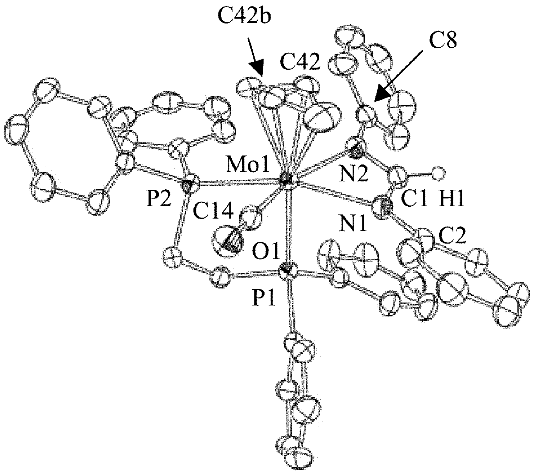


Fig. 3 ORTEP drawing of **6-Mo** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms except for H1 are omitted for clarity.

shorter M(1)–C(14) (1.898(3) Å for **6-Mo** and 1.901(4) Å for **6-W**) and longer C(14)–O(1) bond distances (1.180(3) Å for **6-Mo** and 1.188(4) Å for **6-W**). These results are in good agreement with the CO stretching bands in IR spectra. These complexes **6-Mo** and **6-W** showed one CO stretching band at 1776 and 1766 cm^{-1}, respectively.

The amidinato ligand shows planarity; the sum of angles around N(1) and N(2) in **6-Mo** is 359.7 and 360.0°, respectively. The coordination of the phosphorus group of the dppe ligand located coplanar with the amidinato ligand caused the steric repulsion between the amidinato NPh group and thus the angles around the N(2) nitrogen show larger Mo(1)–N(2)–C(8) and smaller Mo(1)–N(2)–C(1) angles than the corresponding angles around the N(1) nitrogen. The Mo(1)–N(1) distance (2.210(2) Å, *trans* to dppe) is slightly shorter than the Mo(1)–N(2) distance (2.362(2) Å, *trans* to CO). Although the steric repulsion is not negligible, this structural feature might arise from the greater *trans* effect induced by the CO ligand than by the dppe ligand. A similar feature was observed in the Mo–P bond distances. The Mo(1)–P(1) distance (2.5460(8) Å, *trans* to allyl), which is very similar to that in binuclear complex **5-Mo**, is slightly longer than the Mo(1)–P(2) distance (2.4427(6) Å, *trans* to amidinato). Although these values are within the normal range of the Mo–P dative bond distances (2.40–2.57 Å),[18] the difference between these bond distances also might have resulted from the greater *trans* effect induced by the allyl group than by the amidinato group. The structural features of tungsten complex **6-W** were very similar to those of **6-Mo** mentioned above.

It is notable that the allyl groups in complexes **6-Mo** and **6-W** were disordered. The central carbon of the allyl ligand appeared at two sites; one is C(42) and the other is C(42b), as depicted in Fig. 3. Population analyses were undertaken and the ratio of C(42)/C(42b) was found to be *ca.* 0.75/0.25 for **6-Mo** and 0.65/0.35 for **6-W**. In both complexes, the major rotational isomer is the *endo* form, which is defined by the open face of the allyl ligand and the carbonyl ligand being in the same direction. The minor isomer is *exo* form, which is the opposite concerning the allyl and CO ligands (Chart 1). Yih and co-workers have reported the rotational isomers of the η^3-allyl group in dithio–molybdenum complexes bearing a bidentate phosphorus ligand.[19] They studied the relationship between allyl rotation and bidentate phosphorus ligands by X-ray analyses as well as by NMR spectroscopies and revealed that *endo* form is favorable in dithio–molybdenum complexes possessing the dppe ligand. The observation of complexes **6-Mo** and **6-W** mentioned above is consistent with Yih's results.

The non-symmetrical structures of the complexes **6-Mo** and **6-W** prevented from obtaining clear information on their

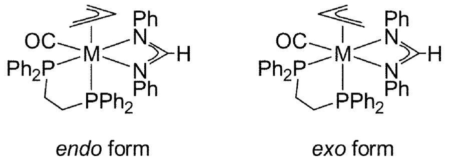


Chart 1

rotational isomers in solution by variable-temperature ^1H NMR measurements. The variable-temperature ^{31}P NMR data are summarized in Table 4. Molybdenum complex **6-Mo** in CD_2Cl_2 at room temperature showed two doublets at 57.1 and 85.3 ppm with a coupling constant of 24.4 Hz and one broad singlet at 59.9 ppm. At higher temperature (90 °C), one set of doublets was observed. The spectrum measured at below 0 °C showed four doublets. At −50 °C, one set of doublets was observed at 58.9 and 86.6 ppm with a coupling constant of 29.0 Hz and the other was seen at 61.2 and 86.5 ppm with a coupling constant of 36.6 Hz. The observed ^{31}P chemical shifts and coupling constants were consistent with the existence of the rotational isomers of the η^3-allyl ligand as has been reported by Yih for the dithio–molybdenum complexes bearing dppe ligands, in that the *endo* form shows a smaller coupling constant (*ca.* 26 Hz) than the *exo* form (*ca.* 39 Hz).[19] Therefore, we concluded that the former doublets can be assigned to *endo* **6-Mo** and the latter to *exo* **6-Mo**. The integration ratio of *endo*/*exo* was 0.75/0.25, which is in good agreement with value obtained by the X-ray diffraction study for **6-Mo** (ratio of 0.75/0.25). In a case of tungsten complex **6-W**, both isomers were observed even at room temperature. At −50 °C, the integration ratio of *endo*/*exo* was 0.70/0.30. This result also conformed to the X-ray analysis of **6-W** (ratio of 0.65/0.35).

Concluding remarks

We investigated the reaction of complex **1** with bidentate ligands such as phen and dppe as a continuation of our systematic research on the reactivity of amidinato(pyridine) complexes of molybdenum and tungsten. In the case of the nitrogen donor, phen, the vacant site needed for the coordinatively unsaturated intermediate was provided by the conversion of the amidinato ligand from η^2- to η^1-coordination. Although it is well known that the amidinato ligand can coordinate to the metal in various fashions, the η^1-coordination mode of the amidinato ligand characterized by X-ray analysis is rare.[12] [13] On the other hand, in the case of the phosphorus donor, dppe, the vacant reaction site is provided by the CO dissociation form the metal to afford monocarbonyl complex **6** *via* dppe-bridged binuclear complex **5**. The different reactivity between phen and dppe might have come from the difference in the π-acceptability of the bidentate ligands. Phen, which is a weaker π-acceptor ligand than dppe,[20] may change the hapticity of the amidinato ligand prior to the liberation of one of the CO ligands, whereas the phosphorus ligand has enough π-acceptability to replace the CO ligand. In these reactions, however, neither CO insertion into the M–N(amidinato) bond (Path B in Scheme 1) nor hapticity change of allyl ligand from η^3- to η^1-fashion (Path A in Scheme 1) has been observed. A further investigation of the reactivity of complex **1** on this line is now in progress.

Experimental

General procedures

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under an atmosphere of dry argon or nitrogen, which was purified by SICAPENT (Merck Co., Inc.), by using standard Schlenk-tube or high-vacuum techniques. All solvents were distilled over appropriate drying agents prior to use. 1,2-Bis(diphenylphosphino)ethane

Table 4 Variable-temperature $^{31}P\{^1H\}$ NMR data for complexes **6-Mo** and **6-W**[a]

	endo **6-Mo**	*exo* **6-Mo**	*endo* **6-W**	*exo* **6-W**
r.t.	57.1 (d, J_{PP} = 24.4 Hz) 85.3 (d, J_{PP} = 24.4 Hz) (*0.70*)	59.9 (br) Overlapped (*0.30*)	52.4 (s, J_{PW} = 216.7 Hz) 62.9 (s, J_{PW} = 251.8 Hz) (*0.65*)	49.9 (br) 59.7 (br) (*0.35*)
90 °C[b]	57.5 (d, J_{PP} = 28.1 Hz) 85.8 (d, J_{PP} = 28.1 Hz)		50.9 (br) 62.2 (br)	
0 °C	57.7 (d, J_{PP} = 27.5 Hz) 85.7 (d, J_{PP} = 27.5 Hz) (*0.70*)	60.3 (d, J_{PP} = 36.6 Hz) 85.8 (d, J_{PP} = 36.6 Hz) (*0.30*)	52.9 (d, J_{PP} = 4.6 Hz, J_{PW} = 219.7 Hz) 63.3 (d, J_{PP} = 4.6 Hz, J_{PW} = 248.7 Hz) (*0.35*)	50.4 (d, J_{PP} = 18.3 Hz, J_{PW} = 210.6 Hz) 60.1 (d, J_{PP} = 18.3 Hz, J_{PW} = 239.6 Hz) (*0.35*)
−50 °C	58.9 (d, J_{PP} = 29.0 Hz) 86.6 (d, J_{PP} = 29.0 Hz) (*0.75*)	61.2 (d, J_{PP} = 36.6 Hz) 86.5 (d, J_{PP} = 36.6 Hz) (*0.25*)	53.7 (s, J_{PW} = 219.7 Hz) 66.3 (s, J_{PW} = 247.2 Hz) (*0.70*)	51.3 (d, J_{PP} = 16.8 Hz, J_{PW} = 215.2 Hz) 60.9 (d, J_{PP} = 16.8 Hz, J_{PW} = 239.6 Hz) (*0.30*)

[a] In CD_2Cl_2 unless otherwise mentioned. Italic numerical values in parentheses indicate integration ratio. Conditions: 161.70 MHz, 5.0 s repetition time and pulse wide 90° (13.0 µs). [b] In toluene.

(dppe)[21] and $[M(\eta^3\text{-allyl})\{\eta^2\text{-}(NC_6H_5)_2CH\}(CO)_2(NC_5H_5)]$ (M = Mo; **1-Mo**, W; **1-W**)[8a] were prepared according to the literature methods. 1,10-Phenanthroline (phen) and 2,2′-bipyridine (bpy) were purchased from Kanto Chemical Co., Inc., and used as received. Other reagents employed in this research were commercially available and used without further purification.

^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on JEOL EX-270, AL-400 and ECA-600 spectrometers at ambient temperature unless otherwise mentioned. PFG-COSY and ^1H–^{31}P PFG-HMBC spectra were measured on JEOL AL-400 and ECA-600 spectrometers, respectively. ^1H and $^{13}C\{^1H\}$ NMR chemical shifts were reported in ppm relative to internal Me_4Si. $^{31}P\{^1H\}$ NMR chemical shifts were recorded in ppm relative to external H_3PO_4. All coupling constants were recorded in Hz. IR spectra were recorded on Perkin-Elmer 1600 FT-IR and a HORIBA FT-730 spectrometers. High resolution mass spectroscopy (HRMS) was recorded on a JEOL JMS-SX102. Elemental analyses were carried out with an LECO CHNS-932.

Preparation of $[Mo(\eta^3\text{-allyl})\{\eta^1\text{-}(NC_6H_5)_2CH\}(CO)_2(\eta^2\text{-phen})]$ (2-Mo)

Complex **1-Mo** (72 mg, 0.15 mmol), phen (32 mg, 0.18 mmol), and CH_2Cl_2 (10 cm^3) were put in a Schlenk tube. After being stirred at room temperature for 0.5 h, the volatiles were removed under reduced pressure. The residual solid was washed with toluene several times, and then dried *in vacuo* to give **2-Mo** as a red solid (75 mg, 0.13 mmol, 87%). Analytically pure **2-Mo**·CH_2Cl_2 was obtained by recrystallization from CH_2Cl_2. Anal. Calc. for $C_{31}H_{26}Cl_2MoN_4O_2$: C, 56.98; H, 4.01; N, 8.57. Found: C, 57.53; H, 4.58; N, 8.55%. IR (ν_{CO}, KBr): 1931, 1842. ^1H NMR (δ, in CD_2Cl_2, at −40 °C): 1.47 (d, J = 9.9 Hz, 2H, allyl-CH_2), 2.72 (tt, J = 9.9, 6.6 Hz, 1H, allyl-CH), 3.16 (d, J = 5.9 Hz, 2H, allyl-CH_2), 5.18 (d, J = 7.3 Hz, 2H, amidinato-Ph), 5.93 (m, 3H, amidinato-Ph), 6.84 (m, 3H, amidinato-Ph), 7.16 (m, 2H, amidinato-Ph), 7.65 (s, 2H, phen), 7.79 (dd, J = 7.9, 4.6 Hz, 2H, phen), 8.32 (dd, J = 7.9, 1.3 Hz, 2H, phen), 9.12 (dd, J = 4.6, 1.3 Hz, 2H, phen), 9.39 (s, 1H, amidinato-CH).

Preparation of $[W(\eta^3\text{-allyl})\{\eta^1\text{-}(NC_6H_5)_2CH\}(CO)_2(\eta^2\text{-phen})]$ (2-W)

Complex **2-W** was prepared from **1-W** (55 mg, 0.099 mmol), phen (21 mg, 0.12 mmol), and CH_2Cl_2 (5 cm^3) in the same manner as that for **2-Mo**. Complex **2-W** was isolated as a red powder (55 mg, 0.084 mmol, 85%). Analytically pure **2-W**·CH_2Cl_2 was obtained by recrystallization from CH_2Cl_2. Anal. Calc. for $C_{31}H_{26}Cl_2N_4O_2W$: C, 50.23; H, 3.54; N, 7.56. Found: C, 50.02; H, 3.69; N, 7.47%. IR (ν_{CO}, KBr): 1921, 1828. ^1H NMR (δ, in CD_2Cl_2, at −60 °C): 1.67 (d, J = 9.2 Hz, 2H, allyl-CH_2), 1.80 (m, 1H, allyl-CH), 3.00 (d, J = 5.9 Hz, 2H, allyl-CH_2), 5.16 (d, J = 7.3 Hz, 2H, amidinato-Ph), 5.91 (m, 3H, amidinato-Ph), 6.88 (d, J = 7.3 Hz, 2H, amidinato-Ph), 7.15 (m, 3H, amidinato-Ph), 7.69 (s, 2H, phen), 7.84 (dd, J = 7.9, 5.3 Hz, 2H, phen), 8.39 (dd, J = 8.6, 1.3 Hz, 2H, phen), 9.20 (dd, J = 5.3, 1.3 Hz, 2H, phen), 9.41 (s, 1H, amidinato-CH).

Preparation of allylamidine (3)

Complex **2-Mo** (50 mg, 0.088 mmol) and DMSO (3 cm^3) were put in a Schlenk tube and then the reaction mixture was heated at 90 °C for 1 h. The resulted umber solution was loaded on an alumina column (ϕ 12 × 100 mm) and eluted with ether–hexane (1 : 8). The pale yellow band was collected and dried *in vacuo* to give **3** as a pale yellow oily material (11 mg, 0.047 mmol, 53%). ^1H NMR (δ, in $CDCl_3$): 4.66 (dt, J = 5.0, 1.6 Hz, 2H, $CH_2{=}CHCH_2$), 5.20 (dd, J = 10.2, 1.6 Hz, 1H, $CH_2{=}CHCH_2$), 5.24 (dd, J = 17.2, 1.6 Hz, 1H, $CH_2{=}CHCH_2$), 6.01 (ddt, J = 17.2, 10.2, 1.6 Hz, 1H, $CH_2{=}CHCH_2$), 7.01–7.38 (m, 10H, C_6H_5), 8.10 (s, 1H, amidine-CH). $^{13}C\{^1H\}$ NMR (δ, in $CDCl_3$): 49.4, 116.5, 120.4, 121.2, 123.3, 124.2, 129.0, 129.4, 133.1, 144.3, 150.1, 151.4. HRMS (EI): Calc. for $C_{16}H_{16}N_2$: m/z 236.1313. Found: 236.1316.

Preparation of $[Mo(\eta^3\text{-allyl})\{\eta^1\text{-}(NC_6H_5)_2CH\}(CO)_2(\eta^2\text{-bpy})]$ (4)

Complex **1-Mo** (50 mg, 0.11 mmol), bpy (24 mg, 0.15 mmol) and CH_2Cl_2 (5 cm^3) were put in a Schlenk tube. After being stirred at room temperature for 1 h, the volatiles were removed under reduced pressure. The residual solid was washed with toluene (2 × 5 cm^3), and then dried *in vacuo* to give **4** as a red solid (46 mg, 0.084 mmol, 76%). Anal. Calc. for $C_{28}H_{24}MoN_4O_2$: C, 61.77; H, 4.44; N, 10.29. Found: C, 61.12; H, 4.22; N, 10.76%. IR (ν_{CO}, KBr): 1928, 1840. ^1H NMR (δ, in CD_2Cl_2, at −50 °C): 6.99–7.28 (m, 10H, Ph), 7.33 (ddd, J = 7.6, 4.9, 1.2 Hz, 2H, bpy), 7.83 (ddd, J = 8.3, 7.6, 1.8 Hz, 2H, bpy), 8.25 (s, 1H, amidinato-CH), 8.38 (ddd, J = 8.3, 1.2, 1.0 Hz, 2H, bpy), 8.63 (ddd, J = 4.9, 1.8, 1.0 Hz, 2H, bpy). The allyl protons were not able to be characterized.

Preparation of $[Mo(\eta^3\text{-allyl})\{\eta^2\text{-}(NC_6H_5)_2CH\}(CO)_2]_2(\mu\text{-dppe})$ (5-Mo)

Complex **1-Mo** (58 mg, 0.12 mmol), dppe (27 mg, 0.068 mmol), and CH_2Cl_2 (5 cm^3) were put in a Schlenk tube. The reaction mixture was stirred at room temperature for several hours and thus an orange solid was precipitated. Hexane (10 cm^3) was added to the reaction mixture. The resulting orange precipitates were isolated by filtration, washed with hexane (3 × 5 cm^3), and dried *in vacuo* to give **5-Mo** (42 mg, 0.036 mmol, 60%). Anal.

Calc. for $C_{62}H_{56}Mo_2N_4O_4P_2$: C, 63.38; H, 4.80; N, 4.77. Found: C, 62.99; H, 4.87; N, 4.68%. IR (ν_{CO}, KBr): 1924, 1843.

Preparation of [W(η^3-allyl){η^2-$(NC_6H_5)_2CH$}$(CO)_2$]$_2$(μ-dppe) (5-W)

Complex **5-W** was prepared from complex **1-W** (57 mg, 0.10 mmol) and dppe (21 mg, 0.053 mmol) in CH_2Cl_2 (5 cm^3) in the same manner as that for **5-Mo**. Complex **5-W** was isolated as an orange powder (43 mg, 0.032 mmol, 60%). Anal. Calc. for $C_{62}H_{56}N_4O_4P_2W_2$: C, 55.13; H, 4.18; N, 4.15. Found: C, 54.59; H, 3.93; N, 4.05%. IR (ν_{CO}, KBr): 1916, 1831.

Preparation of [Mo(η^3-allyl){η^2-$(NC_6H_5)_2CH$}(CO)(η^2-dppe)] (6-Mo)

Method A. Complex **1-Mo** (30 mg, 0.064 mmol), dppe (38 mg, 0.095 mmol) and CH_3CN (10 cm^3) were put in a Schlenk tube. After being refluxed overnight, the volatiles were removed under reduced pressure. The residual solid was treated with hot hexane to afford an orange powder, which was collected and dried *in vacuo* to give **6-Mo** (29 mg, 0.038 mmol, 59%). Analytically pure **6-Mo** was obtained by recrystallization from toluene–hexane as orange crystals containing 0.5 molecules of toluene solvate. Anal. Calc. for $C_{46.5}H_{44}MoN_2OP_2$: C, 69.40; H, 5.51; N, 3.48. Found: C, 69.44; H, 5.61; N, 3.45%. IR (ν_{CO}, KBr): 1776. ^{1}H NMR (δ, in CD_2Cl_2, at −50 °C): *endo* form; 0.45 (t, J = 11.0 Hz, 1H, allyl-CH_2), 1.91 (br, 1H, PCH_2), 2.52–2.88 (m, 3H, PCH_2), 3.00 (br, 1H, allyl-CH_2), 3.32 (d, J = 12.1 Hz, 1H, allyl-CH_2), 4.32 (d, J = 5.5 Hz, 1H, allyl-CH_2), 5.01 (m, 1H, allyl-CH), 5.91 (d, J = 7.7 Hz, 2H, Ph), 6.57 (t, J = 8.2 Hz, 2H, Ph), 7.65 (d, J = 3.3 Hz, 1H, amidinato-CH), 6.79–7.71 (m, 24H, Ph), 7.87 (m, 2H, Ph). *exo* form; 1.91 (br, 1H, PCH_2), 2.24 (d, J = 11.0 Hz, 2H, allyl-CH_2), 2.41 (d, J = 11.5 Hz, 1H, allyl-CH_2), 2.52–2.88 (m, 3H, PCH_2), 4.06 (m, 1H, allyl-CH), 4.47 (m, 1H, allyl-CH_2), 5.99 (d, J = 7.1 Hz, 2H, Ph), 6.79–7.71 (m, 28H, Ph), 7.72 (d, J = 3.8 Hz, 1H, amidinato-CH).

Method B. Complex **5-Mo** (18 mg, 0.015 mmol), dppe (11 mg, 0.027 mmol), and CH_3CN (5 cm^3) were put in a Schlenk tube. After being refluxed for 4 h, the volatiles were removed under reduced pressure. The residual solid was recrystallized from hot hexane to yield **6-Mo** (17 mg, 0.022 mmol, 73%).

Preparation of [W(η^3-allyl){η^2-$(NC_6H_5)_2CH$}(CO)(η^2-dppe)] (6-W)

Method A. Complex **1-W** (48 mg, 0.086 mmol), dppe (47 mg, 0.12 mmol), and toluene (10 cm^3) were put in a Schlenk tube. After being refluxed for 20 h, the volatiles were removed under reduced pressure. The residual solid was recrystallized by toluene–hexane to afford red crystals, which were collected and dried *in vacuo* to give **6-W** containing 0.5 molecules of toluene solvate (38 mg, 0.043 mmol, 50%). Anal. Calc. for $C_{46.5}H_{44}N_2OP_2W$: C, 62.57; H, 4.97; N, 3.14. Found: C, 62.60; H, 5.01; N, 3.15%. IR (ν_{CO}, KBr): 1766. ^{1}H NMR (δ, in CD_2Cl_2, at −50 °C): *endo* form; 0.74 (t, J = 9.9 Hz, 1H, allyl-CH_2), 2.02 (m, 1H, PCH_2), 2.68–2.83 (m, 2H, PCH_2), 2.89 (br, 1H, allyl-CH_2), 3.12 (dt, J = 42.3, 13.2 Hz, 1H, PCH_2), 3.28 (d, J = 11.5 Hz, 1H, allyl-CH_2), 4.21 (m, 1H, allyl-CH), 4.26 (br, 1H, allyl-CH_2), 5.92 (d, J = 7.7 Hz, 2H, Ph), 6.59 (t, J = 8.2 Hz, 2H, Ph), 6.81–7.46 (m, 24H, Ph), 7.88 (t, J = 9.3 Hz, 2H, Ph), 8.32 (d, J = 2.7 Hz, 1H, amidinato-CH). *exo* form; 1.50 (d, J = 9.9 Hz, 1H, allyl-CH_2), 2.02 (m, 2H, allyl-CH_2), 2.38 (m, 1H, PCH_2), 2.56 (m, 1H, PCH_2), 2.68–2.99 (m, 2H, PCH_2), 3.97 (m, 1H, allyl-CH_2), 4.04 (m, 1H, allyl-CH), 6.11 (d, J = 7.7 Hz, 2H, Ph), 6.81–7.46 (m, 24H, Ph), 7.70 (t, J = 9.0 Hz, 2H, Ph), 7.88 (t, J = 9.3 Hz, 2H, Ph), 8.33 (d, J = 3.3 Hz, 1H, amidinato-CH).

Method B. Complex **5-W** (43 mg, 0.032 mmol), dppe (17 mg, 0.043 mmol) and toluene (5 cm^3) were put in a Schlenk tube. The reaction mixture was refluxed for 4 h, and then the mixture was concentrated to the volume of *ca.* 1 cm^3. After addition of hexane (a few drops), the solution was kept in a refrigerator to give red crystals, which were collected by filtration, washed with hexane (3 × 5 cm^3), and dried *in vacuo* yielding **6-W**·0.5PhMe (32 mg, 0.036 mmol, 56%).

Experimental procedure for X-ray crystallography

Suitable single crystals, except for **5-Mo** and **5-W**, were obtained by recrystallization from CH_2Cl_2 (**2-Mo**·CH_2Cl_2), from acetone-d$_6$ (**2-W**), or from toluene–hexane (**6-Mo**·0.5PhMe and **6-W**·0.5PhMe) in a refrigerator and are individually mounted on glass fibers. Single crystals of **5-Mo** and **5-W** were directly obtained from the reaction mixture in CH_2Cl_2 kept in a refrigerator and were individually mounted on glass fibers. Diffraction measurements of all crystals were made on a Rigaku AFC-7R automated four-circle diffractometer by using graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å). The data collections were carried out at −50 °C using the ω–2θ scan technique to a maximum 2θ value of 60.0° for all crystals. Cell constants and an orientation matrix for data collection were determined from 25 reflections with 2θ angles in the range 28.55–29.78° for **2-Mo**, 29.66–30.00° for **2-W**, 29.52–29.96° for **5-Mo**, 29.80–29.99° for **5-W**, 29.69–30.00° for **6-Mo**, and 29.78–29.96° for **6-W**, respectively. Three standard reflections were monitored at every 150 measurements. The data collection was performed on a personal computer. In the reduction of data, Lorentz and polarization corrections and an empirical absorption correction (Ψ scan) were made.

Crystallographic data and the results of measurements are summarized in Table 1. The structures were solved by direct methods (SIR 92)[22] for **2-Mo**, **2-W**, **5-Mo** and **6-Mo**, or by heavy-atom Patterson methods (PATTY)[23] for **5-W** and **6-W**, and expanded using Fourier techniques.[24] All of the non-hydrogen atoms were refined anisotropically. In complexes **2-Mo** and **2-W**, all hydrogen atoms were located from difference Fourier maps and refined isotropically. In complexes **5-Mo**, **5-W**, **6-Mo** and **6-W**, hydrogen atoms were located from difference Fourier maps and refined atomic coordinates. The isotropic thermal parameters of those hydrogen atoms were fixed at about 1.5 times that of the preceding carbon atom. In cases of **6-Mo** and **6-W**, hydrogen atoms of toluene solvate and allyl protons in *exo* form were not assigned. The population of allyl protons in *endo* form conformed to that of the parent carbons. All calculations were performed on an SGI Indy computer using the teXsan crystallographic software package of Molecular Structure Corporation.[25]

CCDC reference numbers 244945–244950.

See http://www.rsc.org/suppdata/dt/b4/b410927a/ for crystallographic data in CIF or other electronic format.

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