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Syntheses and chemistry of Tris(2-pyridyl)phosphine complexes of Group VI transition metals. X-ray structural studies of the molybdenum complexes

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Abstract

Treatment of P(2-py)$_3$ with Mo(CO)$_6$ or M(CO)$_3$(CH$_3$CN)$_3$ (M = Cr, W) in CH$_3$CN affords compounds of the type, P(2-py)$_3$M(CO)$_3$ (**1a**, M = Cr; **1b**, M = Mo; **1c**, M = W). Complex P(2-py)$_3$Mo(CO)$_3$·CH$_2$Cl$_2$ was structurally characterized, and its ORTEP drawing shows an almost perfect octahedral arrangement around the Mo center, and the P(2-py)$_3$ ligand occupying the *facial* position of the octahedron through the coordination of three pyridyl nitrogen atoms. Substitution of CO ligands can take place when treating compounds **1b** and **1c** with one or two equiv. of NOBF$_4$ in CH$_3$NO$_2$ solvent to afford [P(2-py)$_3$M(CO)$_{3-n}$(NO)$_n$](BF$_4$)$_n$ (**2a**, M = Mo, *n* = 1; **2b**, M = W, *n* = 1; **3a**, M = Mo, *n* = 2; **3b**, M = W, *n* = 2). These singly and doubly charged cationic species have been characterized by ^{1}H-, ^{13}C-, ^{31}P-, ^{19}F-NMR and IR spectroscopy, as well as elemental analysis. The CO lability of **3a** and **3b** generated the 16-electron species, [P(2-py)$_3$M(NO)$_2$]$^{2+}$, which binds to most Lewis basic donor ligands to give complexes of the type [P(2-py)$_3$M(L)(NO)$_2$](BF$_4$)$_2$ (L = nitriles, aldehydes). A single crystal of [P(2-py)$_3$M(CH$_3$CH$_2$CN)(NO)$_2$](BF$_4$)$_2$·CH$_3$NO$_2$ was also isolated and structurally characterized. The crystallographic analysis indicated an octahedral arrangement about the Mo metal center. The ^{1}H-NMR downfield shift of the metal-coordinated crotonaldehyde in compounds **4c** and **5c** is used as a qualitative measurement of relative Lewis acidity, and the acid strength of [P(2-py)$_3$M(NO)$_2$]$^{2+}$ is comparable to that of TiCl$_4$ when M = Mo and to BF$_3$ and AlCl$_3$ when M = W. The Diels–Alder reactions between cyclohexadienes and methyl vinyl ketone were catalyzed by 0.3 mol% of [P(2-py)$_3$W(CO)(NO)$_2$](BF$_4$)$_2$ (**3b**) to afford an average 94% conversion and 83% isolated yield. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Group VI transition metals; Molybdenum; X-ray

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1. Introduction

The synthesis of Tris(2-pyridyl)phosphine (P(2-py)$_3$, 2-py = 2-pyridyl) was first reported [1] in 1944 by Davies and Mann as part of a study on the optical resolution of tertiary phosphines. Yet the complexation of P(2-py)$_3$ with metal ions was not reported until 1970 [2]. There has been an increasing usage of P(2-py)$_3$ in inorganic and organometallic chemistry primarily because of its interesting structural feature retaining both phosphorus and nitrogen atoms with versatile coordination possibility. There are four coordination modes found for complexes containing P(2-py)$_3$, namely, P-monodentate [3,4], η^2-*P*,*N*-chelate [5,6a], μ-*P*,*N*-bridge [7] and η^3-*N*,*N*′,*N*″-chelate [8]. Thus, application of P(2-py)$_3$ ligations affords numerous novel and useful complexes. Apart from its characteristics in coordination chemistry, the catalysis aspects of P(2-py)$_3$ for the reactions employing triphenylphosphine have been recently explored [6]. We have focused our interest on the η^3-*N*,*N*′,*N*″-P(2-py)$_3$ ligation, where the P(2-py)$_3$ ligand binds to group VI transition metals at facial position of an octahedron via three pyridyl nitrogen atoms. The η^3-*N*,*N*′,*N*″-chelate has been mostly observed as a π-acceptor ligand in sandwich complexes of first-row transi-

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tion metals with low oxidation state. The electrochemical properties such as the σ- and π-delocalization as well as the π-accepting capability of a series of cobalt complexes containing two η^3-*N*,*N*′,*N*″-chelating ligands have been discussed [9]. These sandwich complexes are generally formulated as $[M(P(2\text{-py})_3)_2]^{2+}$ (M = Mn, Co, Ni, Cu, Zn, Ru) [8a–c]. However, only two examples of half-sandwich complexes have been reported, that is, $ZnP(2\text{-py})_3(\eta^1\text{-}NO_3)(\eta^2\text{-}NO_3)$ [8d] and $RuCl(PPh_3)P(2\text{-py})_3$ [8e].

In this paper, we report our research on the synthesis, characterization, and reactivity of Group VI transition-metal half-sandwich complexes supported by η^3-*N*,*N*′,*N*″-P(2-py)$_3$ ligation. Substitution of the neutral CO ligands in $P(2\text{-py})_3M(CO)_3$ (M = Cr: **1a**, Mo: **1b**, W: **1c**) by the isoelectronic NO$^+$ groups affords cationic species of the type $[P(2\text{-py})_3M(CO)_{3-n}(NO)_n]^{n+}$ ($n = 1$, 2). The dinitrosyl complexes, $[P(2\text{-py})_3M(CO)(NO)_2](BF_4)_2$ (M = Mo: **3a**, W: **3b**), have been proven to be strong Lewis acid precursors. In solution, complexes **3a** and **3b** release their CO and generate 16-electron species of the type $[P(2\text{-py})_3M(NO)_2]^{2+}$, which are capable of binding basic nitriles and aldehydes. Furthermore, **3b** is also active in promoting the Diels–Alder reaction of cyclohexadiene and methyl vinyl ketone. The Diels–Alder reactions of 1,3-butadiene and methyl vinyl ketone [10] as well as the additions of silylated C-nucleophiles to carbonyl compounds [11] have also been observed to be catalyzed by the analogues Lewis acid precursor, $[HC(2\text{-py})_3W(CO)(NO)_2](SbF_6)_2$, where the HC(2-py)$_3$ ligand is an η^3-*N*,*N*′,*N*″ ligand.

Though catalysis using complexes containing pyridylphosphine ligands, $PPh_{3-n}(2\text{-py})_n$ ($n = 1,2$) has developed noticeably in the past two decades [4,12], the application of P(2-py)$_3$ in homogeneous catalysis is still limited [6]. We are therefore interested in exploring the catalytic aspects of P(2-py)$_3$ in homogeneous systems.

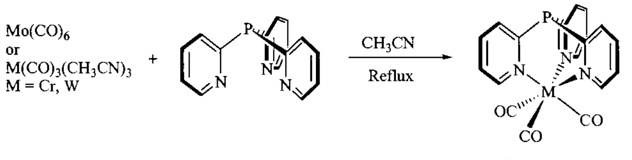
2. Experimental

All manipulations were carried out either by use of standard Schlenk techniques or in a Vacuum Atmospheres glove-box unless specified otherwise. NMR spectra were recorded on a Varian Gemini-200 QNP or a Bruker AMX 400 QNP spectrometer, and chemical shifts were reported relatively to TMS for ^{1}H- and ^{13}C-NMR spectra, 85% H_3PO_4 for ^{31}P-NMR spectra, and $CFCl_3$ for ^{19}F-NMR spectra in $CDCl_3$, CD_3NO_2, CD_3CN and DMSO-*d*$_6$. Infrared spectra were obtained with a Perkin–Elmer 682 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of South Taiwan National Science Council Instrument Center. Mass spectra were obtained on a VG TRIO-2000 spectrometer.

All solvents were dried with use of standard procedures. Crotonaldehyde and methyl vinyl ketone were purified by vacuum-transferred from CaH_2. Cyclohexadiene was used as purchased. All other materials were used as received without further purification. Tris(2-pyridyl)phosphine was prepared by a modification of the reported procedure [6a]. $Cr(CO)_3(CH_3CN)_3$ and $W(CO)_3(CH_3CN)_3$ were prepared by following the literature methods [13].

2.1. Synthesis of P(2-py)$_3$Cr(CO)$_3$ (1a)

A suspension of 0.28 g $Cr(CO)_6$ (1.2 mmol) in 30 ml of CH_3CN was heated at reflux under N_2 for 48 h, tris-2-pyridylphosphine (0.28 g, 1.1 mmol) was then added to the yellow solution. The reaction mixture was heated at reflux for another 12 h. A purple-colored precipitate formed during reflux. After cooling, the resulting solution was concentrated, and the supernatant was decanted and the precipitate was washed with $CHCl_3$ and dried in vacuo overnight to afford P(2-py)$_3$Cr(CO)$_3$. Yield 0.27 g (64%, based on P(2-py)$_3$ added). ^{1}H-NMR ($CDCl_3$, 27°C, 200 MHz): δ 7.15 (t), 7.62 (t), 8.05 (t), 9.55 (d). ^{31}P-NMR ($CDCl_3$, 27°C, 80 MHz): δ −12.4 ppm. IR ($CDCl_3$,): $\nu_{CO} = 1901$ (s), 1777 (br) cm^{-1}. Anal. Calc. for $C_{18}H_{12}N_3O_3PCr$: C, 53.29; H, 3.14; N, 10.21. Found: C, 53.88; H, 3.01; N, 10.47%.



1a, M = Cr
1b, M = Mo
1c, M = W

2.2. Synthesis of P(2-py)$_3$Mo(CO)$_3$ (1b)

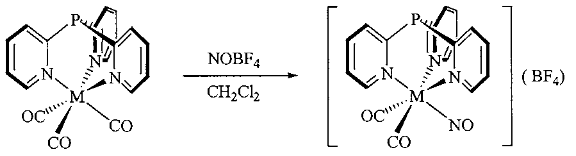
A mixture of Tris-2-pyridyl-phosphine (200 mg, 0.7 mmol) and $Mo(CO)_6$ (200 mg, 0.7 mmol) in 10 ml of CH_3CN was heated at reflux under N_2 for 8 h to afford a red precipitate. The crude product was filtered and washed with petroleum ether, and the solid was dried in vacuo overnight to give red P(2-py)$_3$Mo(CO)$_3$. Yield 288 mg (89%). ^{1}H-NMR ($CDCl_3$, 27°C, 200 MHz): δ 7.20 (t), 7.70 (t), 8.08 (t), 9.45 (d). ^{31}P-NMR ($CDCl_3$, 27°C, 80 MHz): δ −3.2 ppm. IR ($CDCl_3$): $\nu_{CO} = 1908$ (s), 1797 (br) cm^{-1}. Anal. Calc. for $C_{18}H_{12}N_3O_3PMo$: C, 48.35; H, 2.72; N, 9.41. Found: C, 48.56; H, 2.72; N, 9.44%.

2.3. Synthesis of P(2-py)$_3$W(CO)$_3$ (1c)

A suspension of $W(CO)_6$ (220 mg, 0.56 mmol) in 10 ml of CH_3CN was heated at reflux under N_2 for 24 h, Tris-2-pyridylphosphine (136 mg, 0.51 mmol) was then added to the yellow solution. The reaction mixture was heated at reflux for another 12 h. A maroon-colored precipitate formed during reflux. After cooling, the resulting solution was concentrated, and the supernatant was decanted and the precipitate was washed with petroleum ether and dried in vacuo overnight to afford P(2-py)$_3$W(CO)$_3$. Yield 300 mg (61%, based on P(2-py)$_3$ added). ^{1}H-NMR (CDCl$_3$, 27°C, 200 MHz): δ 7.15 (t), 7.75 (t), 8.15 (t), 9.45 (d). ^{31}P-NMR (CDCl$_3$, 27°C, 80 MHz): δ −4.5 ppm. IR (CDCl$_3$): $\nu_{CO} = 1899$ (s), 1784 (br) cm^{-1}. Anal. Calc. for $C_{18}H_{12}N_3O_3PW$: C, 40.49; H, 2.33; N, 7.89. Found: C, 40.55; H, 2.27; N, 7.88%.

2.4. *Synthesis of [P(2-py)$_3$Mo(CO)$_2$(NO)](BF$_4$)* (**2a**)

To a suspension of P(2-py)$_3$Mo(CO)$_3$ (100 mg, 0.225 mmol) in 10 ml of CH$_2$Cl$_2$ was added 1 equiv. of NOBF$_4$ (26 mg, 0.222 mmol). An immediate vigorous gas evolution was observed upon addition of NOBF$_4$. The reaction mixture was allowed to stir at ambient temperature for 1 h. The unreacted P(2-py)$_3$Mo(CO)$_3$ was filtered off from the dark red solution, and the solvent was removed from the filtrate to give an orange–red solid. The solid was then dried in vacuo overnight to give orange–red [P(2-py)$_3$Mo(CO)$_2$-(NO)](BF$_4$). Yield 95 mg (79%). ^{1}H-NMR (CD$_3$CN, 27°C, 200 MHz): δ 7.55–7.65 (m), 8.06–8.18 (m), 8.28–8.41 (*m*), 8.97 (d, $J = 5.12$ Hz), 9.20 (d, $J = 4.76$ Hz). ^{13}C-NMR (d_6-DMSO, 27°C, 100 MHz): δ 222.0 (CO). ^{31}P-NMR (CD$_3$CN, 27°C, 80 MHz): δ −4.75. ^{19}F-NMR (CD$_3$CN, 27°C, 376 MHz): δ −151.3 ppm. IR (KBr): $\nu_{CO} = 2046$ (s), 1940 (br); $\nu_{NO} = 1668$ (s); $\nu_{BF} = 1060$ (br) cm^{-1}. Anal. Calc. for $C_{17}H_{12}BF_4N_4O_3PMo$: C, 38.23; H, 2.30; N, 10.41. Found: C, 38.24; H, 2.26; N, 10.49%.



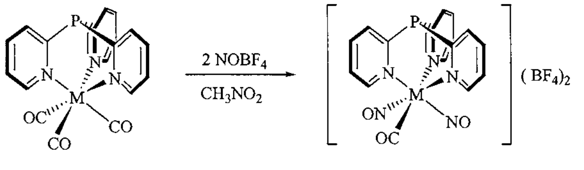
2a, M = Mo
2b, M = W

2.5. *Synthesis of [P(2-py)$_3$W(CO)$_2$(NO)](BF$_4$)* (**2b**)

To a suspension of P(2-py)$_3$W(CO)$_3$ (100 mg, 0.188 mmol) in 10 ml of CH$_2$Cl$_2$ was added 1 equiv. of NOBF$_4$ (22 mg, 0.188 mmol). An immediate vigorous gas evolution was observed upon addition of NOBF$_4$. The reaction mixture was allowed to stir at ambient temperature for 1 h. The suspended impurities were filtered off from the dark purple solution, and the solvent was removed from the filtrate to give a purple solid. The solid was then dried in vacuo overnight to give [P(2-py)$_3$W(CO)$_2$(NO)](BF$_4$). Yield 89 mg (76%). ^{1}H-NMR (CD$_3$CN, 27°C, 200 MHz): δ 7.55–7.65 (m), 8.02–8.20 (m), 8.32–8.46 (*m*), 9.05 (d, $J = 5.12$ Hz), 9.28 (d, $J = 5.12$ Hz). ^{13}C-NMR (d_6-DMSO, 27°C, 100 MHz): δ 222.1 (CO). ^{31}P-NMR (CD$_3$CN, 27°C, 80 MHz): δ −8.07. ^{19}F-NMR (CD$_3$CN, 27°C, 376 MHz): δ −151.3 ppm. IR (KBr): $\nu_{CO} = 2012$ (s), 1912 (br); $\nu_{NO} = 1650$ (s); $\nu_{BF} = 1060$ (br) cm^{-1}. Anal. Calc. for $C_{17}H_{12}BF_4N_4O_3PW$: C, 38.81; H, 1.91; N, 9.01. Found: C, 32.83; H, 1.94; N, 9.01%.

2.6. *Synthesis of [P(2-py)$_3$Mo(CO)(NO)$_2$](BF$_4$)$_2$* (**3a**)

To a suspension of [P(2-py)$_3$Mo(CO)$_3$ (100 mg, 0.225 mmol) in 5 ml of CH$_3$NO$_2$ was added 2 equiv. of NOBF$_4$ (53 mg, 0.454 mmol). An immediate vigorous gas evolution was observed upon addition of NOBF$_4$. The reaction mixture was allowed to stir at ambient temperature for 10 min. The suspended impurities were filtered off from the dark green solution, and dried in vacuo overnight to give green solids of [P(2-py)$_3$Mo(CO)(NO)$_2$](BF$_4$) $_2$. Yield 90 mg (90%). ^{1}H-NMR (CD$_3$NO$_2$, 27°C, 200 MHz): δ 7.87 (m), 8.37 (m), 8.58 (*m*), 9.08 (d), 9.18 (d). ^{31}P-NMR (CD$_3$NO$_2$, 27°C, 80 MHz): δ −5.8 ppm. IR (CD$_3$NO$_2$): $\nu_{CO} = 2037$ (br); $\nu_{NO} = 1839$ (s), 1738 (s); $\nu_{BF} = 1026$ (br) cm^{-1}.



3a, M = Mo
3b, M = W

2.7. *Synthesis of [P(2-py)$_3$W(CO)(NO)$_2$](BF$_4$)$_2$* (**3b**)

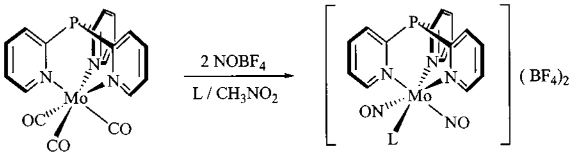
To a suspension of P(2-py)$_3$W(CO)$_3$ (100 mg, 0.188 mmol) in 5 ml of CH$_3$NO$_2$ was added 2 equiv. of NOBF$_4$ (44 mg, 0.376 mmol). An immediate vigorous gas evolution was observed upon addition of NOBF$_4$. The reaction mixture was allowed to stir at ambient temperature for 30 min. The suspended impurities were filtered off from the dark green solution. Recrystallizations of the crude product from CH$_3$NO$_2$–ether solution at −18°C for 24 h gave green crystals of [P(2-py)$_3$W(CO)(NO)$_2$](BF$_4$)$_2$. Yield 75 mg (56%). ^{1}H-NMR (CD$_3$NO$_2$, 27°C, 200 MHz): δ 7.89–7.96 (m), 8.43–8.50 (m), 8.64–8.74 (*m*), 9.25–9.43 (m). ^{13}C-NMR (CD$_3$NO$_2$, 27°C, 50 MHz): δ 192.2 (CO). ^{31}P-NMR (CD$_3$NO$_2$, 27°C, 80 MHz): δ −10.58. ^{19}F-NMR (CD$_3$NO$_2$, 27°C, 188 MHz): δ −151.7 ppm. IR (KBr): $\nu_{CO} = 2148$ (br); $\nu_{NO} = 1844$ (s), 1758 (s); $\nu_{BF} = 1030$ (br) cm^{-1}. Anal. Calc. for $C_{16}H_{12}B_2F_8N_5O_3PW$: C, 26.74; H, 1.78; N, 9.70. Found: C, 27.04; H, 1.70; N, 9.85%.

2.8. Synthesis of $[P(2\text{-}py)_3M(L)(NO)_2](BF_4)_2$, where M = Mo and W; L = CH_3CN and CH_3CH_2CN

A typical procedure for the synthesis of $[P(2\text{-}py)_3M(L)(NO)_2](BF_4)_2$ is described as follows. To a suspension of $P(2\text{-}py)_3Mo(CO)_3$ (50 mg, 0.112 mmol) in 5 ml of CH_3CN was added 2 equiv. of $NOBF_4$ (26 mg, 0.222 mmol). An immediate vigorous gas evolution was observed upon addition of $NOBF_4$. The reaction mixture was allowed to stir at ambient temperature for 30 min. The suspended impurities were filtered off from the dark green solution, and 5 ml of dry diethyl ether (5 ml) was added to the filtrate. The resulting solution was allowed to sit at − 18°C for 24 h to give green crystalline solids of $[P(2\text{-}py)_3Mo(CH_3CN)(NO)_2](BF_4)_2$. Spectroscopic data are given below.

2.8.1. $[P(2\text{-}py)_3Mo(CH_3CN)(NO)_2](BF_4)_2$ (**4a**)

^1H-NMR (CD_3NO_2, 27°C, 200 MHz): δ 7.81–7.91 (m), 8.30–8.40 (m), 8.56–8.72 (*m*), 9.08 (d, $J = 5.12$ Hz), 9.28 (d, $J = 5.20$ Hz), 2.62 (s, CH_3CN). ^{13}C-NMR (CD_3NO_2, 27°C, 50 MHz): δ 136.5 (CH_3CN), 4.3 (CH_3CN). ^{31}P-NMR (CD_3NO_2, 27°C, 80 MHz): δ − 6.26. ^{19}F-NMR (CD_3NO_2, 27°C, 188 MHz): δ − 151.5 ppm. IR (KBr): $\nu_{CN} = 2294$ (br); $\nu_{NO} = 1834$ (s), 1732 (s) cm^{-1}. Anal. Calc. for $C_{17}H_{15}B_2F_8N_6O_2PMo$: C, 28.20; H, 2.10; N, 11.52. Found: C, 28.21; H, 2.09; N, 11.61%.



4a, M = Mo; L = CH_3CN
4b, M = Mo; L = C_2H_5CN
4c, M = Mo; L = $CH_3CH{=}CHCH{=}O$
5a, M = W; L = CH_3CN
5b, M = W; L = C_2H_5CN
5c, M = W; L = $CH_3CH{=}CHCH{=}O$
5d, M = W; L = $(C_6H_5)CH{=}O$

2.8.2. $[P(2\text{-}py)_3Mo(CH_3CH_2CN)(NO)_2](BF_4)_2$ (**4b**)

^1H-NMR (CD_3NO_2, 27°C, 200 MHz): δ 7.81–7.92 (m), 8.29–8.41 (m), 8.52–8.67 (*m*), 9.08 (d, $J = 5.22$ Hz), 9.17 (d, $J = 5.20$ Hz), 2.98 (q, $J = 7.40$ Hz, CH_3CH_2CN), 1.36 (t, $J = 7.62$ Hz, CH_3CH_2CN). ^{13}C-NMR (CD_3NO_2, 27°C, 50 MHz): δ 139.5 (CH_3CH_2CN), 13.8 (CH_3CH_2CN), 9.4 (CH_3CH_2CN). ^{31}P-NMR (CD_3NO_2, 27°C, 80 MHz): δ − 5.91. ^{19}F-NMR (CD_3NO_2, 27°C, 188 MHz): δ − 151.7 ppm. IR (KBr): $\nu_{CN} = 2294$ (br); $\nu_{NO} = 1830$ (s), 1728 (s) cm^{-1}. Anal. Calc. for $C_{19}H_{20}B_2F_8N_7O_4PMo$: C, 31.93; H, 2.83; N, 13.57. Found: C, 32.07 H, 2.81; N, 13.78%.

2.8.3. $[P(2\text{-}py)_3W(CH_3CN)(NO)_2](BF_4)_2$ (**5a**)

^1H-NMR (CD_3NO_2, 27°C, 200 MHz): δ 7.82–7.95 (m), 8.33–8.45 (m), 8.58–8.71 (*m*), 9.17–9.22 (m), 2.66 (s, CH_3CN). ^{13}C-NMR (CD_3NO_2, 27°C, 50 MHz): δ 138.1 (CH_3CN), 4.8 (CH_3CN). ^{31}P-NMR (CD_3NO_2, 27°C, 80 MHz): δ − 10.75. ^{19}F-NMR (CD_3NO_2, 27°C, 188 MHz): δ − 151.3 ppm. IR (KBr): $\nu_{CN} = 2296$ (br); $\nu_{NO} = 1802$ (s), 1716 (s) cm^{-1}. Anal. Calc. for $C_{17}H_{15}B_2F_8N_6O_2PW$: C, 28.20; H, 2.10; N, 11.52. Found: C, 28.21; H, 2.09; N, 11.61%.

2.8.4. $[P(2\text{-}py)_3W(CH_3CH_2CN)(NO)_2](BF_4)_2$ (**5b**)

^1H-NMR (CD_3NO_2, 27°C, 200 MHz): δ 7.82–7.96 (m), 8.34–8.46 (m), 8.52–8.72 (*m*), 9.16–9.22 (m), 3.00 (q, $J = 7.52$ Hz, CH_3CH_2CN), 1.37 (t, $J = 7.50$ Hz, CH_3CH_2CN). ^{13}C-NMR (CD_3NO_2, 27°C, 50 MHz): δ 141.0 (CH_3CH_2CN), 14.1 (CH_3CH_2CN), 9.2 (CH_3CH_2CN). ^{31}P-NMR (CD_3NO_2, 27°C, 80 MHz): δ − 10.71. ^{19}F-NMR (CD_3NO_2, 27°C, 188 MHz): δ − 151.3 ppm. IR (KBr): $\nu_{CN} = 2284$ (br); $\nu_{NO} = 1790$ (s), 1688 (s) cm^{-1}. Anal. Calc. for $C_{18}H_{17}B_2F_8N_6O_2PW$: C, 29.37; H, 2.29; N, 11.16. Found: C, 29.30; H, 2.32; N, 11.39%.

2.9. Reactions of $[P(2\text{-}py)_3M(CO)(NO)_2](BF_4)_2$ with aldehydes, where M = Mo and W; aldehyde = $CH_3CH{=}CHCHO$ and C_6H_5CHO

A typical procedure for the synthesis of $[P(2\text{-}py)_3M(L)(NO)_2](BF_4)_2$ is described as follows. A solution of $P(2\text{-}py)_3Mo(CO)_3$ (50 mg, 0.112 mmol) and $NOBF_4$ (9 mg, 0.084 mmol) in 0.5 ml of CD_3NO_2 was allowed to react for 20 min in a 5 mm Wilmad 528 pp NMR tube equipped with an air-free J. Young Valve. A slight excess of crotonaldehyde (50 µl) was then added into the reaction tube. The solution was allowed to react at room temperature for one day until no starting metal material resonances were observed by the ^1H-NMR. Spectroscopic data is given below.

2.9.1. $[P(2\text{-}py)_3Mo(CH_3CH{=}CHCHO)(NO)_2](BF_4)_2$ (**4c**)

^1H-NMR (CD_3NO_2, 27°C, 200 MHz): δ 7.81–7.95 (m), 8.30–8.45 (m), 8.54–8.69 (m), 8.90–9.05 (m), 9.91 (d, $J = 8.70$ Hz, $CH_3CH{=}CHCHO$), 7.98–8.15 (m, $CH_3CH{=}CHCHO$), 6.64–6.76 (m, $CH_3CH{=}CHCHO$), 2.34 (d, $J = 6.50$ Hz, $CH_3CH{=}CHCHO$). ^{13}C-NMR (CD_3NO_2, 27°C, 50 MHz): δ 211.5 ($CH_3CH{=}CHCHO$), 177.6 ($CH_3CH{=}CHCHO$), 134.4 ($CH_3CH{=}CHCHO$), 21.7 ppm ($CH_3CH{=}CHCHO$).

2.9.2. $[P(2\text{-}py)_3W(CH_3CH{=}CHCHO)(NO)_2](BF_4)_2$ (**5c**)

^1H-NMR (CD_3NO_2 27°C, 200 MHz): δ 7.75–8.00 (m), 8.30–8.45 (m), 8.55–8.72 (m), 8.87 (d, $J = 5.80$ Hz), 9.10 (d, $J = 5.76$ Hz), 9.16–9.22 (m), 9.96 (d, $J = 8.90$ Hz, $CH_3CH{=}CHCHO$), 8.11–8.29 (m, $CH_3CH{=}CHCHO$), 6.70–6.82 (m, $CH_3CH{=}CHCHO$), 2.37 (d, $J = 6.88$ Hz, $CH_3CH{=}CHCHO$). ^{13}C-NMR

(CD_3NO_2, 27 °C, 50 MHz): δ 211.1 ($CH_3CH{=}CH\mathit{C}HO$), 180.7 ($CH_3\mathit{C}H{=}CHC\mathit{H}O$), 134.8 ($CH_3CH{=}\mathit{C}HCHO$), 22.2 ppm ($\mathit{C}H_3CH{=}CHCHO$).

2.9.3. $[P(2\text{-}py)_3W(C_6H_5CHO)(NO)_2](BF_4)_2$ (**5d**)

^{1}H-NMR (CD_3NO_2, 27°C, 200 MHz): δ 10.60 (s, $C_6H_5C\mathit{H}O$), 8.00–8.20 ppm (m, $C_6\mathit{H}_5CHO$).

2.10. Catalytic Diels–Alder reactions of cyclohexadiene and methyl vinyl ketone

All Diels–Alder reactions were carried out in the same manner. In a typical procedure, 10 mg (14.0 μmol) of $[P(2\text{-}py)_3W(CO)(NO)_2](BF_4)_2$ (**3b**) in 10 ml of CH_2Cl_2 was placed in a 25-ml flask. The flask was cooled to 0°C before the addition of 0.4 ml of methyl vinyl ketone (4.8 mmol). Cyclohexadiene (0.53 ml, 5.6 mmol) was then added dropwise to the reaction mixture over 2–3 min. After 24 h, the solution was subjected to a rotary evaporator to remove all volatiles. The crude products were then purified by column chromatography using 20:1 hexane–ethylacetate as eluent. Yield 0.61 g (85%). All Diels–Alder products were identified by NMR comparison to authentic material made as described in the literature. The percentage conversion and isomer ratios were determined by ^{1}H-NMR integration of the enone aldehydic proton and methyl protons of the cyclohexadiene adducts.

2.11. X-ray crystallographic analyses of $P(2\text{-}py)_3Mo(CO)_3{\cdot}CH_2Cl_2$ and $[P(2\text{-}py)_3Mo(CH_3CH_2CN)(NO)_2](BF_4)_2{\cdot}CH_3NO_2$

General operation procedures have been reviewed. Some selected crystallographic data and data collection parameters are summarized in Tables 1 and 2. Suitable single crystals of $P(2\text{-}py)_3Mo(CO)_3{\cdot}CH_2Cl_2$ and $[P(2\text{-}py)_3Mo(CH_3CH_2CN)(NO)_2](BF_4)_2{\cdot}CH_3NO_2$ were grown at −18°C from CH_2Cl_2 and CH_3CH_2CN–CH_3NO_2 solutions, respectively, for X-ray single-crystal structure determination. A crystal of $P(2\text{-}py)_3Mo(CO)_3{\cdot}CH_2Cl_2$ with dimensions of 0.40 × 0.50 × 0.55 mm^3 and a crystal of $[P(2\text{-}py)_3Mo(CH_3CH_2CN)(NO)_2](BF_4)_2{\cdot}CH_3NO_2$ with dimensions of 0.15 × 0.25 × 0.35 mm^3 were mounted in capillary tubes under a nitrogen atmosphere. Data were recorded at ambient temperature on an Enraf–Nonius CAD4 diffractometer using graphite-monochromatized Mo–K$_\alpha$ radiation. Unit-cell dimensions were determined from 25 well-centered reflections ($20.84 \leq 2\theta \leq 38.10°$) for $P(2\text{-}py)_3Mo(CO)_3{\cdot}CH_2Cl_2$, and from 25 well-centered reflections ($14.74 \leq 2\theta \leq 29.36°$) for $[P(2\text{-}py)_3Mo(CH_3CH_2CN)(NO)_2](BF_4)_2{\cdot}CH_3NO_2$. Three intensity standards were measured for every 1 h of exposure time and declined systematically by 2% during the course of the measurements. Both structures were solved using the Patterson heavy-atom method [14] and refined by a full-matrix least-square procedure using NRCVAX [15] to reveal the positions of molybdenum atoms. Systematic absences and subsequent least-squares refinement indicated a monoclinic $C2/c$ space group for $P(2\text{-}py)_3Mo(CO)_3{\cdot}CH_2Cl_2$ and a monoclinic $P2_1/c$ space group for $[P(2\text{-}py)_3Mo(CH_3CH_2CN)(NO)_2](BF_4)_2{\cdot}CH_3NO_2$. The remaining atoms were located in suc-

Table 1
Crystallographic data for $P(2\text{-}py)_3Mo(CO)_3{\cdot}CH_2Cl_2$ and $[P(2\text{-}py)_3Mo(CH_3CH_2CN)(NO)_2](BF_4)_2{\cdot}CH_3NO_2$

Formula	$C_{19}H_{14}N_3O_3MoPCl_2$	$C_{19}H_{20}N_7O_4MoB_2F_8$
FW	530.15	710.93
Diffractometer	Nonius	Nonius
Space group	Monoclinic, $C2/c$	Monoclinic, $P2_{1/c}$
a (Å)	26.304 (6)	17.754 (4)
b (Å)	10.8570 (20)	11.204 (3)
c (Å)	17.087 (6)	16.025 (3)
β (°)	121.53 (3)	115.292 (18)
V (Å^3)	4159.6 (19)	2882.2 (12)
Z	8	4
$D_{calc.}$ (g cm^{-3})	1.693	1.638
λ (Å)	0.7107	0.7107
F(000)	2101	1410
Unit cell detn: # (2θ range)	25 (20.84–38.10°)	25 (14.74–29.36°)
Scan type	θ /2θ	θ/2θ
Scan width (°)	2 (0.65+ 0.35 tan θ)	2 (0.60+ 0.35 tan θ)
Scan speed (° min^{-1})	2.06–8.24	2.06–8.24
2θ (max)	50.0	50.0
h, k, l ranges	(−31; 26), (0; 12), (0; 20)	((21; 19), (0; 13), (0; 18)
μ (cm^{-1})	6.319	5.713
Crystal size (mm)	0.40 × 0.50 × 0.55	0.15 × 0.25 × 0.35
Transmission	0.881; 1.000	0.965; 1.000
Temperature (K)	298	298
Number of meas reflections	3730	5064
Number of obsed reflections ($I > 2.0\sigma(I)$)	3105	2326
Number of unique reflections [a]	3645	5064
R_f; R_w ($I > 2.0\sigma(I)$) [b]	0.029; 0.030	0.064; 0.063
R_f; R_w (all reflections)	0.037; 0.036	0.147; 0.067
Goodness of-fit [c]	1.47	2.88
Refinement program	NRCVAX	NRCVAX
Number of atoms	47	62
Number of refined parameters	272 (3105 out of 3645)	380 (2326 out of 5064)
Minimize function	$\Sigma(w \mid F_o - F_c\mid^2)$	$\Sigma(w\mid F_o - F_c\mid^2)$
(Δ/σ) max	0.0117	0.0372
Residual in final D-map max min (e Å^3)	−0.730; 0.770	(0.690; 0.810

[a] Three standard reflns monitored every 3600 s, intensity variation <2%, solvent: CH_2Cl_2 (disorder) for $[P(2\text{-}py)_3Mo(CO)_3]{\cdot}CH_2Cl_2$. Anion: $2BF_4^-$, Solvent: CH_3NO_2 for $[P(2\text{-}py)_3Mo(CH_3CH_2CN)(NO)_2](BF_4)_2{\cdot}CH_3NO_2$.

[b] $R_f = \Sigma(F_o - F_c)/\Sigma(F_o)$; $R_w = [\Sigma(w(F_o - F_c)^2)/\Sigma(wF_o^2)]^{1/2}$.

[c] Goodness of-fit $[\Sigma(w(F_o - F_c)^2)/(\text{number of reflections} - \text{number of parameters})]^{1/2}$.

Table 2
Selected bond distances (Å) and angles (°) for P(2-Py)$_3$Mo(CO$_3$)·CH$_2$Cl$_2$

Bond distances			
Mo–N(1)	2.279(3)	Mo–N(2)	2.282(3)
Mo–N(3)	2.266(3)	Mo–C(1)	1.951(4)
Mo–C(2)	1.928(4)	Mo–C(3)	1.938(4)
C(1)–O(1)	1.158(4)	C(2)–O(2)	1.170(4)
C(3)–O(3)	1.165(4)		
Bond angles			
N(1)–Mo–N(2)	84.56(10)	N(1)–Mo–N(3)	84.12(10)
N(2)–Mo–N(3)	83.74(10)	N(1)–Mo–C(1)	95.89(12)
N(1)–Mo–C(2)	92.84(12)	N(2)–Mo–C(1)	93.39(13)
N(2)–Mo–C(3)	97.49(13)	N(3)–Mo–C(2)	96.56(12)
N(3)–Mo–C(3)	92.51(12)	N(1)–Mo–C(3)	175.85(12)
N(2)–Mo–C(2)	177.35(12)	N(3)–Mo–C(1)	177.12(13)
C(1)–Mo–C(2)	86.32(15)	C(1)–Mo–C(3)	87.60(14)
C(2)–Mo–C(3)	85.13(15)		

ceeding difference Fourier syntheses. Hydrogen atoms were located and added to the structures, but their position were not refined.

3. Results and discussion

*3.1. Synthesis and characterization of P(2-py)$_3$M(CO)$_3$, where M = Cr (**1a**), Mo (**1b**) and W (**1c**)*

The reactions of P(2-py)$_3$ and 1 equiv. of M(CO)$_3$(CHCN)$_3$, where M = Cr and W, or Mo(CO)$_6$ in CH$_3$CN resulted in the formation of complexes P(2-py)$_3$M(CO)$_3$ (**1a**–**c**). The infrared spectra of **1a**–**c** showing two ν_{CO} bands (**1a**: 1901, 1777; **1b**: 1908, 1797, and **1c**: 1899, 1784 cm^{-1}) suggested that complexes **1a**–**c** held a C_{3v} symmetry. As compared with the CO stretching frequency for CO gas (2143 cm^{-1}), the ν_{CO} found for **1a**–**c** were lower in energy due to a certain degree of metal-to-ligand π-back bonding. Only one set of pyridyl protons (between δ 7.15–9.55 ppm) with a ratio of 1:1:1:1 in the ^{1}H-NMR spectra of **1a**–**c** indicated a η^3-*N*,*N'*,*N''*-P(2-py)$_3$ coordination. Complexes **1a**–**c** gave only one phosphorus resonance in their ^{31}P-NMR spectra. The phosphorus chemical shift at δ − 4.5 ppm for **1c** indicated no sign of P–W interaction.

Transparent purple crystals of P(2-py)$_3$Mo(CO)$_3$·CH$_2$Cl$_2$ suitable for X-ray crystallographic analysis were obtained from the recrystallization of **1b** in CH$_3$CN + CH$_2$Cl$_2$ solution. The ORTEP drawing of P(2-py)$_3$Mo(CO)$_3$·CH$_2$Cl$_2$ (Fig. 1) shows an almost perfect octahedral arrangement around the Mo center, and the P(2-py)$_3$ ligand is occupying at the *facial* position of the octahedron through the coordination of three pyridyl nitrogen atoms with three N–Mo–C angles of 175.85, 177.35, and 177.12° and three Mo–N bonds of 2.279, 2.282 and 2.266 Å in length (Table 2).

*3.2. Synthesis and characterization of [P(2-py)$_3$M(CO)$_2$(NO)](BF$_4$), where M = Mo (**2a**) and W (**2b**)*

The reaction of NO$^+$ with low-valent transition-metal complexes has been widely employed in the synthesis of nitrosyl complexes of both molybdenum and tungsten [16,17]. The treatment of **1a** and **1b** with 1 equiv. of NOBF$_4$ in CH$_2$Cl$_2$ resulted in immediate gas evolution to afford complexes **2a** and **2b**. The ^{1}H-NMR spectra of both **2a** and **2b** showing two sets of pyridyl protons with a ratio of 2:1 indicated that the C_{3v} symmetry was no longer present. The higher CO stretching frequencies (**2a**: 2046, 1940 and **2b**: 2012, 1912 cm^{-1}) than those found for complexes **1a**–**c** suggested a weaker M–CO interaction. However, complexes **2a** and **2b** still possessed rather high stability against further CO ligand replacement in most coordinating solvent systems. In addition to the CO stretching bands, the strong NO stretching bands at 1668 and 1650 cm^{-1} for **2a** and **2b** respectively were typical for linear M–N–O bonding mode [18].

*3.3. Synthesis and characterization of [P(2-py)$_3$M(CO)(NO)$_2$](BF$_4$)$_2$, where M = Mo (**3a**) and W (**3b**)*

Subsequent substitution of the second CO ligand can be achieved by treating complexes **2a** and **2b** with a further 1 equiv. of NOBF$_4$ in CH$_3$NO. Alternatively, complexes **3a** and **3b** can also be synthesized by the direct reaction of **1a**–**b** and 2 equiv. of NOBF$_4$ in CH$_3$NO$_2$. The ^{1}H-NMR spectra of both **3a** and **3b** showing two sets of pyridyl protons with a ratio of 2:1 indicated that the C_{3v} symmetry was no longer present.

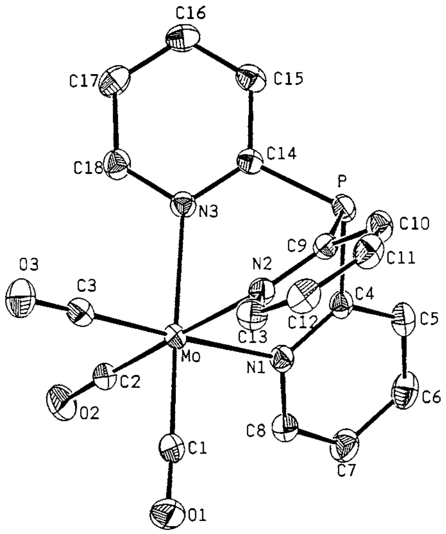


Fig. 1. ORTEP drawing of P(2-py)$_3$Mo(CO)$_3$·CH$_2$Cl$_2$ showing the atom-labeling scheme used. Note that the CH$_2$Cl$_2$ molecule has been omitted for clarity.

The only infrared ν_{CO} band at 2037 and 2148 cm^{-1} for **3a** and **3b**, respectively, was very close to that of free CO, and was higher in energy than those found for **1a**, **1b**, **2a**, and **2b**. Apparently, these high CO stretching frequencies were attributed to the coordination of two NO^+ ligands. Thus, an expected weak M–CO interaction could facilitate the loss of CO in the presence of a suitable coordinating ligand. In addition to the CO stretching bands, two strong NO stretching bands at 1839, 1738 cm^{-1} and 1844, 1785 cm^{-1} for **3a** and **3b**, respectively, were typical for *cis* dinitrosyl complexes with linear M–N–O bonding modes [17,18]. As implied in the infrared spectral data, complexes **3a** and **3b** possessed a characteristic feature of strong CO lability when dissolving in donor solvents. Presumably, the loss of CO generated a 16-electron species, $[P(2\text{-}py)_3M(NO)_2]^{2+}$; the metal–anion interaction, therefore, became possible without the presence of coordinating solvent. Many examples of organometallic complexes of weakly coordinating anions, e.g. BF_4^-, PF_6^-, AsF_6^- and SbF_6^-, have been reported [19,20]. However, the infrared absorption bands of ν_{BF} at 1026 and 1030 cm^{-1} for **3a** and **3b**, respectively, indicated no asymmetric broadening of the BF_4^-. Moreover, subsequent ^{19}F-NMR studies for **3b** showing two equivalent BF_4^- anions (δ −151.7 ppm) at room temperature suggested no direct M–F–BF_3 interaction [10]. Apparently, the hard BF_4^- anions in **3a** and **3b** did not bind to soft metal centers in the presence of coordinating solvents.

The CO lability in complexes **3a** and **3b** enables the isolation of a series of complexes, $[P(2\text{-}py)_3M(L)(NO)_2](BF_4)_2$ (L = nitriles, aldehydes). At ambient temperature, the facile CO loss of **3a** and **3b** in the presence of nitriles resulted in the formation of complexes $[P(2\text{-}py)_3M(CH_3CN)(NO)_2](BF_4)_2$ (**4a**, M = Mo; **5a**, M = W) and $[P(2\text{-}py)_3M(CH_3CH_2CN)(NO)_2](BF_4)_2$ (**4b**, M = Mo; **5b**, M = W). A total conversion of **4a** and **5a** to **4b** and **5b** can be accomplished within hours in the presence of a stoichiometric amount of CH_3CN. Transparent green crystals of $[P(2\text{-}py)_3Mo(CH_3CH_2CN)(NO)_2](BF_4)_2\cdot CH_3NO_2$ suitable for X-ray crystallographic analysis were obtained from the recrystallization of **3a** in CH_3CH_2CN/CH_3NO_2 (1:1) solutions. The ORTEP drawing of $[P(2\text{-}py)_3Mo(CH_3CH_2CN)(NO)_2](BF_4)_2\cdot CH_3NO_2$ (Fig. 2) shows an almost perfect octahedral arrangement around the Mo center, and the $P(2\text{-}py)_3$ ligand occupies the *facial* position of the octahedron through the coordination of three pyridyl nitrogen atoms. The almost linear Mo–N–O arrangement with the angles M–N–O of 175.0 and 177.0° (Table 3) indicates the two NO^+ ligands are *cis* to each other.

A similar chemistry has also been observed when **3a** and **3b** were treated with Lewis basic organic carbonyl compounds. In the presence of excess amounts of aldehydes, the $[P(2\text{-}py)_3M(NO)_2](BF_4)_2$–crotonaldehyde adducts **4c** (M = Mo) and **5c**, (M = W) as well as $[P(2\text{-}py)_3W(NO)_2](BF_4)_2$–benzaldehyde adduct **5d** can be spectroscopically analyzed by NMR. Attempts to isolate these aldehyde adducts failed, probably because the relative basicities of these aldehydes were not strong enough, as can be seen in the isolated $[P(2\text{-}py)_3M(NO)_2](BF_4)_2$–nitrile adducts **4a**–**b** and **5a**–**b**.

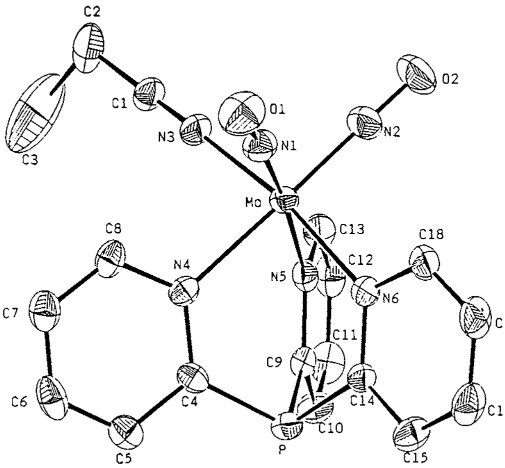


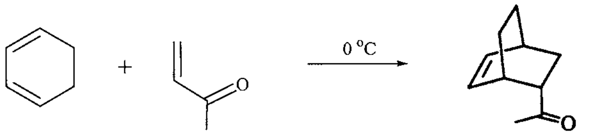
Fig. 2. ORTEP drawing of $[P(2\text{-}py)_3Mo(CH_3CH_2CN)(NO)_2](BF_4)_2\cdot CH_3NO_2$ showing the atom-labeling scheme used. Note that CH_3NO_2 and BF_4^- have been omitted for clarity.

3.4. Lewis acidity and reactivity of $[P(2\text{-}py)_3W(CO)(NO)_2](BF_4)_2$ (3b)

Organometallic Lewis acids are of great importance in the catalysis of carbon–carbon bond formation reactions because the steric bulk of the supporting ligands

Table 3
Selected bond distances (Å) and angles (°) for $[P(2\text{-}py)_3Mo(CH_3CH_2CN)(NO)_2](BF_4)_2\cdot CH_3NO_2$

Bond distances			
Mo–N(1)	1.820(9)	Mo–N(2)	1.819(9)
Mo–N(3)	2.149(8)	Mo–N(4)	2.202(9)
Mo–N(5)	2.206(8)	Mo–N(6)	2.160(8)
N(1)–O(1)	1.155(12)	N(2)–O(2)	1.147(13)
N(3)–C(1)	1.112(13)	C(1)–C(2)	1.464(16)
C(2)–C(3)	1.59(3)		
Bond angles			
N(1)–Mo–N(2)	90.6(5)	N(1)–Mo–N(3)	94.3(4)
N(1)–Mo–N(4)	89.1(4)	N(1)–Mo–N(5)	175.0(4)
N(1)–Mo–N(6)	93.1(3)	N(2)–Mo–N(3)	92.9(4)
N(2)–Mo–N(4)	178.1(3)	N(2)–Mo–N(5)	94.4(4)
N(2)–Mo–N(6)	94.0(4)	N(3)–Mo–N(4)	85.2(3)
N(3)–Mo–N(5)	85.8(3)	N(3)–Mo–N(6)	169.8(3)
N(4)–Mo–N(5)	85.9(3)	N(4)–Mo–N(6)	87.9(3)
N(5)–Mo–N(6)	86.2(3)	Mo–N(1)–O(1)	177.0(10)
Mo–N(2)–O(2)	178.5(9)	Mo–N(3)–C(1)	178.5(9)



Catalyst loading (**3b**, mol %)	Solvent	Time (hrs)	endo : exo	% conversion	Yield (%)
0.3	CH_2Cl_2	24	99 : 1	95	85
0.3	CH_3NO_2	15	99 : 1	93	81

Scheme 1.

and the electronic character of the metals can offer influential effects on the rate and selectivity. The Lewis acidities of complexes **3a** and **3b** are reflected in their facile formation of nitrile (**4a**, **4b**, **5a**, **5b**) and aldehyde adducts (**4c**, **5c**, **5d**). The method developed by Childs et al. [21a] and Hersh and co-workers [21b] took the ^{1}H-NMR chemical shift differences of the 3-position hydrogen of crotonaldehyde before and after coordinated to a Lewis acid as a relative scale to determine the acid strength. In our system, the complexation of crotonaldehyde provided downfield shifts of $\Delta\delta$ 1.01 ppm and $\Delta\delta$ 1.18 ppm for **3a** and **3b**, respectively, and the acidities of **3a** and **3b** were found to be comparable to those of $TiCl_4$ ($\Delta\delta$ 1.03 ppm) and BF_3 ($\Delta\delta$ 1.17 ppm) and $AlCl_3$ ($\Delta\delta$ 1.23 ppm), respectively. Accordingly, we looked into the study of Lewis acid reactivity of complex **3b** for the classical Diels–Alder catalysis. As indicated in Scheme 1, complex **3b** has shown potential activity in promoting the cycloaddition reaction of cyclohexadiene and methyl vinyl ketone. With a loading of 0.3 mol% of **3b**, the cycloaddition reactions provided an average of 94% conversion with a 99% endo-selectivity, while the corresponding thermal reaction only afforded a less than 5% conversion at 0°C. An average 83% isolated yield of the Diels–Alder adduct was obtained when the reaction mixtures were purified by column chromatography.

The polydiene is often observed as a potential side-product of Lewis acid-catalyzed Diels–Alder reactions. However, at a reaction temperature of 0°C, no polymeric materials were observed in the NMR spectroscopic analysis nor insoluble precipitates formed during the course of **3b**-catalyzed Diels–Alder reactions of cyclohexadiene and methyl vinyl ketone. The reactivities, kinetic and mechanistic insights of the catalysis will be subjected to further investigation.

4. Supplementary information

Tables of crystal data, complete bond angles and distances, atomic coordinates, and equivalent displacement coefficients for $P(2\text{-py})_3Mo(CO)_3 \cdot CH_2Cl_2$ (17 pages) and $[P(2\text{-py})_3Mo(CH_3CH_2CN)(NO)_2](BF_4)_2 \cdot CH_3NO_2$ (23 pages). Ordering information is given on any current masthead page.

Acknowledgements

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