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(CH3CN)3 (M = Cr, W) in CH3CN affords compounds of the type, P(2-py)3M(CO)3 (1a, M = Cr; 1b, M = Mo; 1c, M = W). Complex P(2-py)3Mo(CO)3·CH2Cl2 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 NOBF4 in CH3NO2 solvent to afford [P(2-py)3M(CO)3n(NO)n]n(BF4)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 1H-, 13C-, 31P-, 19F-NMR and IR spectroscopy, as well as elemental analysis. The CO lability of 3a and 3b generated the 16-electron species, [P(2-py)3M(NO)2]2, which binds to most Lewis basic donor ligands to give complexes of the type [P(2-py)3M(L)(NO)2](BF4)2 (L = nitriles, aldehydes). A single crystal of [P(2-py)3M(CH3CH2CN)(NO)2](BF4)2·CH3NO2 was also isolated and structurally characterized. The crystallographic analysis indicated an octahedral arrangement about the Mo metal center. The 1H-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)3W(NO)2]2 is comparable to that of TiCl4 when M = Mo and to BF3 and AlCl3 when M = W. The Diels–Alder reactions between cyclohexadienes and methyl vinyl ketone were catalyzed by 0.3 mol% of [P(2-py)3W(CO)(NO)2](BF4)2 (3b) to afford an average 94% conversion and 83% isolated yield. © 1999 Elsevier Science S.A. All rights reserved.

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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], η2-P,N-chelate [5,6a], μ-P,N-bridge [7] and η3-N,N’,N”-chelate [8]. Thus, application of P(2-py), 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 η1-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 η1-N,N’,N”-chelate has been mostly observed as a π-acceptor ligand in sandwich complexes of first-row transi-
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 η1-N,N',N''-chelating ligands have been discussed [9]. These sandwich complexes are generally formulated as [M(P(2-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-py)3(η1-N,NO3)(η1-N,NO3) [8d] and RuCl(PPh3)P(2-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 η1-N,N',N''-P(2-py)3 ligation. Substitution of the neutral CO ligands in P(2-py)3M(CO)3 (M = Cr, Mo: 1b, W: 1c) by the isoelectronic NO+ groups affords cationic species of the type [P(2-py)3M(NO)2](n)(n) (n = 1, 2). The dinitrosyl complexes, [P(2-py)3M(CO)(NO)]2BF4, (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-py)3M(NO)]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 precursors, [HC(2-py)3W(CO)3]2 (SbF6)2, where the HC(2-py)3 ligand is an η1-N,N',N''-delocalized ligand.

Though catalysis using complexes containing pyridylphosphine ligands, PPh3-n(2-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 1H- and 13C-NMR spectra, 85% H3PO4 for 31P-NMR spectra, and CFC13 for 19F-NMR spectra in CDCl3, CD3NO2, CD3CN and DMSO-d6. 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 CaH2. 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(CH3CN)3 and W(CO)3(CH3CN)3 were prepared by following the literature methods [13].

2.1. Synthesis of P(2-py)3Cr(CO)3 (1a)

A suspension of 0.28 g Cr(CO)6 (1.2 mmol) in 30 ml of CH3CN was heated at reflux under N2 for 48 h, tris-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 CHCl3 and dried in vacuo overnight to afford P(2-py)3Cr(CO)3. Yield 0.27 g (64%, based on P(2-py)3). 1H-NMR (CDCl3, 27°C, 200 MHz): δ 1.46 (d), 6.28 (t), 7.62 (t), 8.05 (t), 9.56 (d). 31P-NMR (CDCl3, 27°C, 80 MHz): δ = 12.4 ppm. IR (CDCl3, v): νCO = 1901 (s), 1908 (br) cm−1. Anal. Calc. for C18H12N3O3PMo: C, 53.88; H, 3.01; N, 10.47%.

2.2. Synthesis of P(2-py)3Mo(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 CH3CN was heated at reflux under N2 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)3Mo(CO)3. Yield 288 mg (89%). 1H-NMR (CDCl3, 27°C, 200 MHz): δ 7.20 (t), 7.70 (t), 8.08 (t), 9.45 (d). 31P-NMR (CDCl3, 27°C, 80 MHz): δ = 32 ppm. IR (CDCl3, v): νCO = 1908 (s), 1797 (br) cm−1. Anal. Calc. for C18H12N3O3PMo: C, 53.29; H, 3.14; N, 10.21. Found: C, 53.88; H, 3.01; N, 9.44%.

2.3. Synthesis of P(2-py)3W(CO)3 (1c)

A suspension of W(CO)6 (220 mg, 0.56 mmol) in 10 ml of CH3CN was heated at reflux under N2 for 24 h,
Tris-2-pyridyldisphenine (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),W(CO),). Yield 300 mg (61%, based on P(2-py), added). 1H-NMR (CDCl3, 27°C, 200 MHz): δ 7.15 (t), 7.75 (t), 8.15 (t), 9.45 (d). 13C-NMR (CDCl3, 27°C, 80 MHz): δ = −4.5 ppm. IR (KBr): νCO = 1899 (s), 1784 (br) cm⁻¹. Anal. Calc. for C14H12B2F8N5O3PW: C, 32.83; H, 1.94; N, 9.01%. Found: C, 32.83; H, 2.27; N, 10.49%.

2.4. Synthesis of [P(2-py),Mo(CO),(NO)](BF4)2 (2a)

To a suspension of P(2-py),Mo(CO), (100 mg, 0.225 mmol) in 5 ml of CH3NO2 was added 2 equiv. of NOBF4 (53 mg, 0.454 mmol). An immediate vigorous gas evolution was observed upon addition of NOBF4. 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 the solvent was removed from the filtrate to give a green solid. The solid was then dried in vacuo overnight to give [P(2-py),W(CO),(NO)](BF4). Yield 89 mg (76%). 1H-NMR (CD3CN, 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). 13C-NMR (d6-DMSO, 27°C, 100 MHz): δ = 222.1 (CO). 31P-NMR (CD3CN, 27°C, 80 MHz): δ = −8.07. 19F-NMR (CD3CN, 27°C, 376 MHz): δ = −151.3 ppm. IR (KBr): νCO = 2012 (s), 1912 (br); νNO = 1650 (s); νBF = 1060 (br) cm⁻¹. Anal. Calc. for C14H12B2F4N4O3PMo: C, 38.23; H, 2.30; N, 10.41. Found: C, 38.24; H, 2.26; N, 10.49%.

2.5. Synthesis of [P(2-py),W(CO),(NO)](BF4)2 (2b)

To a suspension of P(2-py),W(CO), (100 mg, 0.188 mmol) in 10 ml of CH3Cl2 was added 1 equiv. of NOBF4 (26 mg, 0.222 mmol). An immediate vigorous gas evolution was observed upon addition of NOBF4. 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),W(CO),(NO)](BF4). Yield 95 mg (79%). 1H-NMR (CD3CN, 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). 13C-NMR (d6-DMSO, 27°C, 100 MHz): δ = 222.0 (CO). 31P-NMR (CD3CN, 27°C, 80 MHz): δ = −4.75. 19F-NMR (CD3CN, 27°C, 376 MHz): δ = −151.3 ppm. IR (KBr): νCO = 2046 (s), 1940 (br); νNO = 1668 (s); νBF = 1060 (br) cm⁻¹. Anal. Calc. for C14H12B2F4N4O3PW: C, 32.83; H, 2.50; N, 10.41. Found: C, 32.84; H, 2.26; N, 10.49%.

2.6. Synthesis of [P(2-py),Mo(CO),(NO)](BF4)2 (3a)

To a suspension of P(2-py),Mo(CO), (100 mg, 0.225 mmol) in 5 ml of CH3NO2 was added 2 equiv. of NOBF4 (53 mg, 0.454 mmol). An immediate vigorous gas evolution was observed upon addition of NOBF4. 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),Mo(CO),(NO)](BF4). Yield 90 mg (90%). 1H-NMR (CD3CN, 27°C, 200 MHz): δ 7.87 (m), 8.37 (m), 8.58 (m), 9.08 (d), 9.18 (d). 31P-NMR (CD3NO2, 27°C, 80 MHz): δ = −5.8 ppm. IR (CD3NO2): νCO = 2037 (br); νNO = 1839 (s), 1758 (s); νBF = 1026 (br) cm⁻¹.

2.7. Synthesis of [P(2-py),W(CO),(NO)](BF4)2 (3b)

To a suspension of P(2-py),W(CO), (100 mg, 0.188 mmol) in 5 ml of CH3NO2 was added 2 equiv. of NOBF4 (44 mg, 0.376 mmol). An immediate vigorous gas evolution was observed upon addition of NOBF4. 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 CH3NO2–ether solution at −18°C for 24 h gave green crystals of [P(2-py),W(CO),(NO)](BF4). Yield 75 mg (56%). 1H-NMR (CD3NO2, 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). 13C-NMR (CD3NO2, 27°C, 50 MHz): δ = 192.2 (CO). 31P-NMR (CD3NO2, 27°C, 80 MHz): δ = 10.58. 19F-NMR (CD3NO2, 27°C, 188 MHz): δ = 151.7 ppm. IR (KBr): νCO = 2148 (br); νNO = 1844 (s), 1758 (s); νBF = 1030 (br) cm⁻¹. Anal. Calc. for C14H12B2F4N4O3PW: 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-py)$_3$M(3CH$_2$CN)(NO)$_3$](BF$_4$)$_2$, where $M$ = Mo and W; $L$ = CH$_3$CN and CH$_2$CH$_2$CN

A typical procedure for the synthesis of [P(2-py)$_3$M(L)(NO)$_3$](BF$_4$)$_2$ is described as follows. To a suspension of P(2-py)$_3$Mo(CO)$_3$ (50 mg, 0.112 mmol) in 5 ml of CH$_3$CN 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-py)$_3$Mo(CH$_3$CN)(NO)$_3$](BF$_4$)$_2$. Spectroscopic data are given below.

2.8.1. [P(2-py)$_3$Mo(CH$_3$CN)(NO)$_3$](BF$_4$)$_2$ (4a)

$^1$H-NMR (CD$_3$NO$_2$, 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$_3$CN). $^{13}$C-NMR (CD$_3$NO$_2$, 27°C, 50 MHz): δ 136.5 (CH$_3$CN), 4.3 (CH$_2$CH$_2$CN). $^{31}$P-NMR (CD$_3$NO$_2$, 27°C, 80 MHz): δ −6.26. $^{19}$F-NMR (CD$_3$NO$_2$, 27°C, 188 MHz): δ −151.5 ppm. IR (KBr): $v_{CN}$ = 2294 (br); $v_{NO}$ = 1834 (s), 1732 (s) cm$^{-1}$. Anal. Calc. for C$_{18}$H$_{17}$B$_2$F$_8$N$_6$O$_2$PW: C, 28.20; H, 2.10; N, 11.52. Found: C, 28.21; H, 2.09; N, 11.61%.

2.8.2. [P(2-py)$_3$Mo(CH$_2$CH$_2$CN)(NO)$_3$](BF$_4$)$_2$ (4b)

$^1$H-NMR (CD$_3$NO$_2$, 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$_3$CH$_2$CN), 1.36 (t, $J$ = 7.62 Hz, CH$_2$CH$_2$CN). $^{13}$C-NMR (CD$_3$NO$_2$, 27°C, 50 MHz): δ 139.5 (CH$_3$CH$_2$CN), 13.8 (CH$_2$CH$_2$CN), 9.4 (CH$_3$CH$_2$CN). $^{31}$P-NMR (CD$_3$NO$_2$, 27°C, 80 MHz): δ −5.91. $^{19}$F-NMR (CD$_3$NO$_2$, 27°C, 188 MHz): δ −151.7 ppm. IR (KBr): $v_{CN}$ = 2294 (br); $v_{NO}$ = 1830 (s), 1728 (s) cm$^{-1}$. Anal. Calc. for C$_{31}$H$_{39}$B$_2$F$_8$N$_6$O$_2$PW: C, 31.93; H, 2.83; N, 13.57. Found: C, 32.07 H, 2.81; N, 13.78%.

2.8.3. [P(2-py)$_3$W(CH$_3$CN)(NO)$_3$](BF$_4$)$_2$ (5a)

$^1$H-NMR (CD$_3$NO$_2$, 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$_3$CN). $^{13}$C-NMR (CD$_3$NO$_2$, 27°C, 50 MHz): δ 138.1 (CH$_3$CN), 4.8 (CH$_3$CN). $^{31}$P-NMR (CD$_3$NO$_2$, 27°C, 80 MHz): δ −10.75. $^{19}$F-NMR (CD$_3$NO$_2$, 27°C, 188 MHz): δ −151.3 ppm. IR (KBr): $v_{CN}$ = 2296 (br); $v_{NO}$ = 1802 (s), 1716 (s) cm$^{-1}$. Anal. Calc. for C$_{31}$H$_{39}$B$_2$F$_8$N$_6$O$_2$PW: C, 31.93; H, 2.83; N, 13.57. Found: C, 32.07 H, 2.81; N, 13.78%.

2.8.4. [P(2-py)$_3$W(CH$_3$CH$_2$CN)(NO)$_3$](BF$_4$)$_2$ (5b)

$^1$H-NMR (CD$_3$NO$_2$, 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$_3$CH$_2$CN), 1.37 (t, $J$ = 7.50 Hz, CH$_2$CH$_2$CN). $^{13}$C-NMR (CD$_3$NO$_2$, 27°C, 50 MHz): δ 141.0 (CH$_3$CH$_2$CN), 14.1 (CH$_3$CH$_2$CN), 9.2 (CH$_2$CH$_2$CN). $^{31}$P-NMR (CD$_3$NO$_2$, 27°C, 80 MHz): δ −10.71. $^{19}$F-NMR (CD$_3$NO$_2$, 27°C, 188 MHz): δ −151.3 ppm. IR (KBr): $v_{CN}$ = 2284 (br); $v_{NO}$ = 1790 (s), 1688 (s) cm$^{-1}$. Anal. Calc. for C$_{31}$H$_{39}$B$_2$F$_8$N$_6$O$_2$PW: C, 31.93; H, 2.83; N, 13.57.

2.9. Reactions of [P(2-py)$_3$M(3CO)(NO)$_3$](BF$_4$)$_2$ with aldehydes, where $M$ = Mo and W; aldehyde = CH$_3$CH=CHCHO and CH$_2$CHCHO

A typical procedure for the synthesis of [P(2-py)$_3$M(L)(NO)$_3$](BF$_4$)$_2$ is described as follows. A solution of P(2-py)$_3$Mo(CO)$_3$ (50 mg, 0.112 mmol) and NOBF$_4$ (9 mg, 0.084 mmol) in 0.5 ml of CD$_3$NO$_2$ was allowed to react for 20 min in a 5 mm Wilmad 528 ppm 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 $^1$H-NMR. Spectroscopic data is given below.

2.9.1. [P(2-py)$_3$Mo(CH$_3$CH=CHCHO)(NO)$_3$](BF$_4$)$_2$ (4c)

$^1$H-NMR (CD$_3$NO$_2$, 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$_3$CH=CHCHO), 7.98–8.15 (m, CH$_2$CH=CHCHO), 6.64–6.76 (m, CH$_3$CH=CHCHO), 2.34 (d, $J$ = 6.50 Hz, CH$_2$CH=CHCHO). $^{13}$C-NMR (CD$_3$NO$_2$, 27°C, 50 MHz): δ 211.5 (CH$_3$CH=CHCHO), 177.6 (CH$_3$CH=CHCHO), 134.4 (CH$_2$CH=CHCHO), 21.7 ppm (CH$_3$CH=CHCHO).

2.9.2. [P(2-py)$_3$W(CH$_3$CH=CHCHO)(NO)$_3$](BF$_4$)$_2$ (5c)

$^1$H-NMR (CD$_3$NO$_2$, 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$_3$CH=CHCHO), 8.11–8.29 (m, CH$_2$CH=CHCHO), 6.70–6.82 (m, CH$_2$CH=CHCHO), 2.37 (d, $J$ = 6.88 Hz, CH$_2$CH=CHCHO). $^{13}$C-NMR
(CD$_3$NO$_2$, 27 °C, 50 MHz); δ 211.1 (CH$_3$CH–CHCHO), 180.7 (CH$_3$CH–CHCHO), 134.8 (CH$_3$CH–CHCHO), 22.2 ppm (CH$_3$CH–CHCHO).

2.9.3. [P(2-py)$_2$W(C$_6$H$_5$CHO)(NO)$_2$](BF$_4$)$_2$ (5d)

$^{1}$H-NMR (CD$_3$NO$_2$, 27°C, 200 MHz); δ 10.60 (s, C$_6$H$_5$CHO), 8.00–8.20 ppm (m, C$_6$H$_5$CHO).

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-py)$_2$W(C$_6$H$_5$CHO)(NO)$_2$](BF$_4$)$_2$ (3b) in 10 ml of CH$_2$Cl$_2$ 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-py)$_2$Mo(CO)$_3$CH$_2$Cl$_2$ and [P(2-py)$_2$Mo(CH$_3$CH$_2$CN)(NO)$_2$](BF$_4$)$_2$:CH$_3$NO$_2$

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-py)$_2$Mo(CO)$_3$CH$_2$Cl$_2$ and [P(2-py)$_2$Mo(CH$_3$CH$_2$CN)(NO)$_2$](BF$_4$)$_2$:CH$_3$NO$_2$ were grown at −18°C from CH$_2$Cl$_2$ and CH$_3$CH$_2$CN–CH$_3$NO$_2$ solutions, respectively, for X-ray single-crystal structure determination. A crystal of [P(2-py)$_2$Mo(CO)$_3$CH$_2$Cl$_2$]$_3$ with dimensions of 0.40 × 0.50 × 0.55 mm$^3$ and a crystal of [P(2-py)$_2$Mo(CH$_3$CH$_2$CN)(NO)$_2$](BF$_4$)$_2$:CH$_3$NO$_2$ 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 ≤ 2θ ≤ 38.10°) for P(2-py)$_2$Mo(CO)$_3$CH$_2$Cl$_2$, and from 25 well-centered reflections (14.74 ≤ 2θ ≤ 29.36°) for [P(2-py)$_2$Mo(CH$_3$CH$_2$CN)(NO)$_2$](BF$_4$)$_2$:CH$_3$NO$_2$. 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-py)$_2$Mo(CO)$_3$CH$_2$Cl$_2$ and a monoclinic $P2_1$/$c$ space group for [P(2-py)$_2$Mo(CH$_3$CH$_2$CN)(NO)$_2$](BF$_4$)$_2$:CH$_3$NO$_2$. The remaining atoms were located in suc-

| Table 1 Crystallographic data for P(2-py)$_2$Mo(CO)$_3$CH$_2$Cl$_2$ and [P(2-py)$_2$Mo(CH$_3$CH$_2$CN)(NO)$_2$](BF$_4$)$_2$:CH$_3$NO$_2$

| Formula | C$_{10}$H$_{18}$N$_2$O$_{10}$MoPCl$_2$ | C$_{10}$H$_{18}$N$_2$O$_{10}$MoB$_2$F$_8$
| 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$^3$) | 41596.19 | 28822.12
| Z | 8 | 4
| D$_{calc}$ (g cm$^{-3}$) | 1.693 | 1.638
| ϵ (Å) | 0.7107 | 0.7107
| F(000) | 2101 | 1410
| Unit cell detn. | 25 (20.84–38.10°) | 25 (14.74–29.36°)
| (2θ range) | # | #
| Scan type | 0/2θ | 0/2θ
| Scan width (°) | 2 (0.65+ | 2 (0.60+
| | 0.35 tan δ) | 0.35 tan δ)
| 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 | 3730 | 5064
| Number of reflections | 3105 | 2326
| Number of unique reflections$^a$ | 3645 | 5064
| R$_I$: R$_F$ (I > 2σ(I))$^b$ | 0.029; 0.030 | 0.064; 0.063
| R$_I$: R$_e$ (all reflections)$^c$ | 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 | 3645 | 5064
| Minimize function | Σ(w | F$_o$− F$_c$ |²) | Σ(w | F$_o$− F$_c$ |²)
| (A/σ) max | 0.0117 | 0.0372
| Residual in final D-map | −0.730; 0.770 | (0.690; 0.810
| max min (e Å$^3$) | |

$^a$ Three standard reflns monitored every 3600 s, intensity variation <2%, solvent: CH$_2$Cl$_2$ (disorder) for [P(2-py)$_2$Mo(CO)$_3$]CH$_2$Cl$_2$. Anion: 2BF$_4$-, Solvent: CH$_3$NO$_2$ for [P(2-py)$_2$Mo(CH$_3$CH$_2$CN)(NO)$_2$](BF$_4$)$_2$:CH$_3$NO$_2$.

$^b$ R$_I$ = Σ(F$_o$− F$_c$)/Σ(F$_o$); R$_e$ = [Σ(w(F$_o$− F$_c$)²)]²/Σ(wF$_o$²)$^{1/2}$.

$^c$ Goodness-of-fit [Σ(w(F$_o$− F$_c$)²)]/(number of reflections − number of parameters)$^{1/2}$.
3. Results and discussion

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

The reactions of \(\text{P}(2\text{-py})_3\) and 1 equiv. of \(\text{M(CO)}_6(\text{CHCN})_3\), where \(\text{M} = \text{Cr} \) and \(W\), or \(\text{Mo(CO)}_6\) in \(\text{CH}_2\text{CN}\) resulted in the formation of complexes \(\text{P}(2\text{-py})_3\text{M(CO)}_3(1\text{a}–\text{c})\). The infrared spectra of \(1\text{a}–\text{c}\) showing two \(v_{\text{CO}}\) bands \((1\text{a}: 1901, 1777; 1\text{b}: 1908, 1797,\) and \(1\text{c}: 1899, 1784 \text{ cm}^{-1}\) suggested that complexes \(1\text{a}–\text{c}\) held a \(C_3v\) symmetry. As compared with the CO stretching frequency for CO gas (2143 cm\(^{-1}\)), the \(v_{\text{CO}}\) found for \(1\text{a}–\text{c}\) were lower in energy due to a certain degree of metal-to-ligand \(\pi\)-back bonding. Only one set of pyridyl protons (between \(\delta 7.15–9.55 \text{ ppm}\) with a ratio of 1:1:1:1 in the \(^1\text{H}-\text{NMR}\) spectra of \(1\text{a}–\text{c}\) indicated a \(\eta^3-N',N'',N'''\)-\(\text{P}(2\text{-py})_3\) coordination. Complexes \(1\text{a}–\text{c}\) gave only one phosphorus resonance in their \(^{31}\text{P}\)-NMR spectra. The phosphorus chemical shift at \(\delta -4.5 \text{ ppm}\) for \(1\text{c}\) indicated no sign of \(P–W\) interaction.

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

3.2. Synthesis and characterization of \(\text{P}(2\text{-py})_3\text{M(CO)}_3(\text{NO})_2(\text{BF}_4)_2\), where \(\text{M} = \text{Mo} (2\text{a})\) and \(W (2\text{b})\)

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 \(1\text{a} \) and \(1\text{b}\) with 1 equiv. of NOBF\(_4\) in CH\(_2\)Cl\(_2\) resulted in immediate gas evolution to afford complexes \(2\text{a}\) and \(2\text{b}\). The \(^1\text{H}-\text{NMR}\) spectra of both \(2\text{a}\) and \(2\text{b}\) 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 (\(2\text{a}: 2046, 1940\) and \(2\text{b}: 2012, 1912 \text{ cm}^{-1}\) than those found for complexes \(1\text{a}–\text{c}\) suggested a weaker M–CO interaction. However, complexes \(2\text{a}\) and \(2\text{b}\) 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 \(2\text{a}\) and \(2\text{b}\) respectively were typical for linear M–N–O bonding mode [18].
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-py)\(_3\)M(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\(_{\mathrm{BF}}\) 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\(_4\) 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-py)\(_3\)M(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-py)\(_3\)M(CH\(_3\)CN)(NO)\(_2\)](BF\(_4\))\(_2\) (4a, M = Mo; 5a, M = W) and [P(2-py)\(_3\)M(CH\(_3\)CH\(_2\)CN)(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\(_3\)CN. Transparent green crystals of [P(2-py)\(_3\)Mo(CH\(_3\)CH\(_2\)CN)(NO)\(_2\)](BF\(_4\))\(_2\)-CH\(_3\)NO\(_2\) suitable for X-ray crystallographic analysis were obtained from the recrystallization of 3a in CH\(_3\)CN/CH\(_3\)NO\(_2\) (1:1) solutions. The ORTEP drawing of [P(2-py)\(_3\)Mo(CH\(_3\)CH\(_2\)CN)(NO)\(_2\)](BF\(_4\))\(_2\)-CH\(_3\)NO\(_2\) (Fig. 2) shows an almost perfect octahedral arrangement around the Mo center, and the P(2-py) 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-py)\(_3\)M(NO)\(_2\)](BF\(_4\))\(_2\)-crotonaldehyde adducts 4c (M = Mo) and 5c, (M = W) as well as [P(2-py)\(_3\)W(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-py)\(_3\)Mo(NO)\(_2\)](BF\(_4\))\(_2\)-nitrile adducts 4a–b and 5a–b.

### 3.4. Lewis acidity and reactivity of [P(2-py)\(_3\)W(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>
<thead>
<tr>
<th>Bond distances (Å) and angles (°) for <a href="BF(_4)">P(2-py)(_3)Mo(CH(_3)CH(_2)CN)(NO)(_2)</a>(_2)-CH(_3)NO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bond distances</strong></td>
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<tr>
<td>Mo–N(1)</td>
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<tr>
<td>Mo–N(3)</td>
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<tr>
<td>Mo–N(5)</td>
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<td>N(1)–O(1)</td>
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<td>N(3)–C(1)</td>
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<td>C(2)–C(3)</td>
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<tr>
<td><strong>Bond angles</strong></td>
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<td>N(1)–Mo–N(4)</td>
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<td>N(3)–Mo–N(6)</td>
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<td>N(4)–Mo–N(5)</td>
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<tr>
<td>N(5)–Mo–N(6)</td>
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<tr>
<td>Mo–N(2)–O(2)</td>
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</tbody>
</table>
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 hydrogen of crotonaldehyde before and after coordination influenced effects on the rate and selectivity. The Lewis and the electronic character of the metals can offer distances, atomic coordinates, and equivalent displacements, 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-py)$_3$Mo(CO)$_3$CH$_2$Cl$_2$ (17 pages) and [P(2-py)$_3$Mo(CH$_3$CH$_2$CN)(NO)$_2$]([BF$_4$]$_2$

CH$_3$NO$_2$ (23 pages). Ordering information is given on any current masthead page.

Acknowledgements

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References

[14] For detailed references, see supplementary material of crystallographic analyses.
[26] For detailed references, see supplementary material of crystallographic analyses.
[37] For detailed references, see supplementary material of crystallographic analyses.