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Synthesis, Characterization, and Highly Selective Ethylene Dimerization to 1-Butene of [O⁻NX]Ni(II) Complexes†

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A series of nickel(II) complexes have been synthesized and characterized. Molecular structure analysis exhibits that a square planar geometry around nickel is adopted. Upon activation with MAO, these nickel(II) complexes are efficient in catalyzing the ethylene dimerization, providing 1-butene with an activity of up to 1.4×10^7 g/(mol•h•atm). The heteroatoms of the sidearm in the complexes were proved to have great impact on the activity and selectivity of 1-butene.

Keywords nickel complexes, ethylene dimerization, 1-butene, selectivity

Introduction

Organonickel complexes have attracted much attention in the filed of olefin polymerization and oligomerization.[1] And tremendous advances were achieved in both industry and academic field.[2] For example, SHOP catalyst, developed by Keim *et al*., can efficiently convert ethylene into value added α-olefins, which has become one of the largest applications of homogeneous catalysis by a transition metal.[3-6] However, of all the nickel complexes developed, we noticed that bidentate ligands were involved in most cases, probably because of either a square planar geometry or a tetrahedral geometry around nickel being considered suitable to meet the requirement of the olefin coordination polymerization.[7-10] Though a few examples of nickel complexes based on tridentate ligands have been reported for this purpose,[11-13] either low activity or low selectivity towards α-olefin was always observed. Recently, Braunstein *et al*. described a bis(oxazolinyl)phenyl phosphonite nickel complex used to promote oligomerization of ethylene with an activity up to 1.1×10^5 g/(mol(Ni)•h•atm) in the presence of $AlEtCl_2$ with the selectivity for α-butene being up to 21%.[11] Casagrande *et al*. documented that tridentate pyrazolyl nickel complexes were efficient catalysts for the ethylene dimerization.[12] Very rencently, by employing the abovementioned tridentate pyrazolyl nickel complexes, they obtained butenes in an activity of 5.3×10^4 g/(mol(Ni)•h•atm) along with 81% selectivity for 1-butene under the optimized conditions.[12b] We have been interested in the olefin coordination polymerization and oligomerization, and a series of new metal complexes were applied successfully in ethylene (co)polymerization,[14] in which the nickel complexes derived from *N*-[(1*H*-pyrrol-2-yl)methylene]-2-(diphenylphosphino)benzenamine were found active to polymerize the norbornene.[15] Recently, we designed a kind of nickel complexes derived from tridentate ligands [ONS], which are highly active [up to 14.25×10^6 g/(mol(Ni)•h•atm)] in catalyzing the ethylene dimerization to provid 1-butene with up to ＞99% selectivity. In this paper we wish to report the results.

Experimental

All manipulations of air- and/or moisture-sensitive compounds were performed under nitrogen atmosphere using standard Schlenk techniques. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian XL-300 MHz or 400 MHz spectrometer with TMS as the internal standard. Mass spectra were obtained using an HP5959A spectrometer. IR spectra were recorded using an Nicolet AV-360 spectrometer. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry, Chinese Acadamy of Sciences. X-ray crystallographic data were collected using a Bruker AXSD8 X-Ray diffractometer. Toluene, THF, hexane and dichloromethane were treated with solvent purification MB SPS-800 for MBRAUN glove box systems prior to use. Methylaluminoxane (MAO) was purchased from Akzo Chemical as an 1.5 mol/L

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toluene solution. Polymerization-grade ethylene was purified before use. Gas chromatographic analyses were performed on an Agilent 7890A gas chromatograph using an HP Pona column (50 m, 0.2 mm diameter, 0.5 μm film thickness).

Synthesis of the ligands

Ligands **L1**—**L5**,[14f] **L7**[14f] and $NiPhCl(PPh_3)_2$[17] were prepared according to the reported procedure.

(*Z*)-3-(2-(Cyclohexylthio)ethylamino)-1,3-diphenylprop-2-en-1-one (L6) To a solution of 1,3-diphenylpropane-1,3-dione (11.62 g, 51.8 mmol) and 2-(cyclohexylthio)ethanamine (8.24 g, 51.8 mmol) in toluene (60 mL) was added 4-methylbenzenesulfonic acid hydrate (0.78 g, 4.1 mmol) at room temperature. The flask was equipped with a water separator. After refluxing for 1 d, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel to give product as yellow solid 8.3 g. Yield 46%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 11.45 (s, 1H), 7.89 (d, J=6.3 Hz, 2H), 7.44—7.38 (m, 8H), 5.78 (s, 1H, C=CH), 3.38 (q, J=7.1 Hz, 2H), 2.63 (t, J=7.2 Hz, 2H), 2.45 (brs, 1H, S-CH), 1.81—1.57 (m, 5H), 1.25—1.17 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 88.5, 166.3, 140.0, 135.4, 130.7, 129.4, 128.5, 128.1, 127.6, 127.0, 93.8, 44.8, 43.3, 33.5, 30.5, 26.0, 25.6; IR (KBr) v: 3055, 2925, 2848, 1605, 1582, 1553, 1339, 782, 765, 746, 690 cm^{-1}; MS (EI) m/z: 365 (M^+), 236 (M—CH_2SCy). HRMS (EI) calcd for $C_{23}H_{27}NOS$ (M^+) 365.1813, found 365.1813. Anal. calcd for $C_{23}H_{27}NOS$: C 75.57, H 7.45, N 3.83; found C 75.68, H 7.40, N 3.85.

(*Z*)-5,5,5-Trifluoro-4-(2-(isopropylthio)ethylamino)pent-3-en-2-one (L8) The same procedure as that for **L6**. Pale-yellow oil (34%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 11.22 (brs, 1H), 5.35 (s, 1H, C=CH), 3.55 (q, J=6.6 Hz, 2H, N-CH_2), 3.00—2.91 (m, 1H, S-CH), 2.77 (t, J=6.9 Hz, 2H), 2.12 (s, 3H), 1.29 (d, J=6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 175.2, 174.8, 169.1, 119.3, 115.5, 89.3, 43.4, 35.0, 29. 9, 23.0, 19.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ: −7.08; IR (KBr) v: 2964, 2928, 2869, 1619, 1593, 1277, 1250, 1185, 1136, 741, 727 cm^{-1}; MS (EI) m/z: 255 (M^+), 166 (M—CH_2SPr-*i*). HRMS (EI) calcd for $C_{10}H_{16}F_3NOS$ (M^+) 255.0905, found 255.0905. Anal. calcd for $C_{10}H_{16}F_3NOS$: C 47.05, H 6.32, N 5.49; found C 47.54, H 6.38, N 5.59.

(*Z*)-3-(2-(Dimethylamino)ethylamino)-1,3-diphenylprop-2-en-1-one (L9) The same procedure as that for **L6**. Pale-yellow solid (80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 11.40 (s, 1H, NH), 7.90—7.88 (m, 2H), 7.47—7.36 (m, 8H), 5.76 (s, 1H), 3.29 (q, J=6.3 Hz, 2H, N-CH_2), 2.43 (t, J=6.6 Hz, 2H), 2.21 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 187.9, 166.1, 140.0, 135.4, 130.3, 129.1, 128.2, 127.8, 127.3, 126.7, 93.1, 59.0, 45.2, 42.5; IR (KBr) v: 3419, 2818, 2767, 1595, 1567, 1481, 1334, 1064, 1023, 839, 784, 752, 714, 693, 682 cm^{-1}; MS (EI) m/z: 294 (M^+), 58 (NMe_2). HRMS (EI) calcd for $C_{19}H_{22}N_2O$ (M^+) 294.1732, found 294.1732. Anal. calcd for $C_{19}H_{22}N_2O$: C 77.52, H 7.53, N 9.52; found C 77.57, H 7.52, N 9.54.

(*Z*)-3-(2-(Diphenylphosphino)ethylamino)-1,3-diphenylprop-2-en-1-one (L10) The same procedure as that for **L6**. Pale-yellow solid (47%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: (s, 1H, NH), 7.89—7.86 (m, 2H), 7.40—7.25 (m, 18H), 5.74 (s, 1H, C=CH), 3.34—3.28 (m, 2H, N-CH_2), 2.32—2.27 (m, 2H, P-CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 188.2, 166.2, 140.0, 137.2, 137.0, 135.1, 132.4, 132.2, 130.6, 129.3, 128.6, 128.4, 128.3, 128.0, 127.4, 126.9, 93.6, 41.7, 41.3, 30.2, 30.1; ^{31}P NMR (121 MHz, $CDCl_3$) δ: −20.78; IR (KBr) v: 3051, 2932, 2865, 1594, 1566, 1408, 1289, 817, 785, 753, 747, 738, 695 cm^{-1}; MS (EI) m/z: 435 (M^+), 330 (M—PhCO). HRMS (EI) calcd for $C_{29}H_{26}NOP$ (M^+) 435.1752, found 435.1752. Anal. calcd for $C_{29}H_{26}NOP$: C 79.98, H 6.02, N 3.22; found C 79.95, H 6.24, N 3.02.

(*Z*)-3-(2-Phenoxyethylamino)-1,3-diphenylprop-2-en-1-one (L11) The same procedure as that for **L6**. Yellow oil (60%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 11.52 (s, 1H, NH), 7.90—7.87 (m, 2H), 7.43—7.36 (m, 8H), 7.29—7.23 (m, 2H), 6.97—6.86 (m, 3H), 5.80 (s, 1H, C=CH), 4.03 (t, J=6.3 Hz, 2H), 3.61 (q, J=5.9 Hz, 2H, O-CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 188.5, 166.5, 158.1, 140.0, 135.2, 130.6, 129.4, 129.3, 128.4, 128.0, 127.7, 126.9, 120.9, 114.4, 93.9, 66.8, 43.7; IR (KBr) v: 3060, 2930, 1595, 1569, 1332, 1243, 1060, 813, 777, 751, 692 cm^{-1}; MS (EI) m/z: 343 (M^+), 250 (M—PhO). HRMS (EI) calcd for $C_{23}H_{21}NO_2$ (M^+) 343.1575, found 343.1572. Anal. calcd for $C_{23}H_{21}NO_2$: C 80.44, H 6.16, N 4.08; found C 80.45, H 6.07, N 4.17.

(*Z*)-1,3-Diphenyl-3-(pyridin-2-ylmethylamino)-prop-2-en-1-one (L12) The same procedure as that for **L6**. Yellow solid (60%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: (s, 1H, NH), 8.57 (d, J=4.2 Hz, 1H); 7.93 (d, J=5.4 Hz, 2H), 7.70—7.66 (m, 1H), 7.43—7.16 (m, 10H), 5.89 (s, 1H, C=CH), 4.57 (d, J=5.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 188.4, 166.2, 157.2, 149.1, 139.7, 136.5, 135.0, 130.5, 129.3, 128.3, 127.9, 127.3, 126.8, 121.9, 120.5, 93.8, 49.7; IR (KBr) v: 3057, 3014, 2911, 1594, 1571, 1333, 812, 799, 778, 763, 745, 726, 690 cm^{-1}; MS (EI) m/z: 314 (M^+), 209 (M—PhCO). HRMS (EI) calcd for $C_{21}H_{18}N_2O$ (M^+) 314.1419, found 314.1418. Anal. calcd for $C_{21}H_{18}N_2O$: C 80.23, H 5.77, N 8.91; found C 80.19, H 5.80, N 8.83.

Typical procedure for the synthesis of the Ni(II) complexes (1 as an example)

To a solution of **L1** (0.31 g, 1.05 mmol) in toluene (10 mL) at −78 ℃ was added dropwise a solution of *n*-BuLi (0.42 mL, 1.05 mmol, 2.5 mol/L in hexane) over 10 min. The resulting mixture was allowed to warm to room temperature and stirred for 2 h. After removing the solvent under reduced pressure, the resulting solid was mixed with $NiPhCl(PPh_3)_2$ (0.71 g, 1.02 mmol) at golvebox and then cooled toluene (−30 ℃) was added. The resulting mixture solution was stirred overnight and then was filtered and concentrated. The yellow solid was collected at −30 ℃.

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[(1*Z*,3*Z*)-3-(2-(Methylthio)ethylimino)-1,3-diphenylprop-1-en-1-olate]NiPh (1) Yield: 0.39 g (91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.68 (d, J=6.6 Hz, 2H), 7.55 (d, J=6.6 Hz, 2H), 7.43—7.18 (m, 8H), 7.03—6.90 (m, 3H), 5.71 (s, 1H, C=CH), 3.37—3.31 (m, 1H), 3.25—3.17 (m, 1H), 2.62—2.55 (m, 1H), 2.25—2.21 (m, 1H), 2.07 (s, 3H, S-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 172.3, 167.3, 149.1, 140.7, 139.2, 137.3, 129.1, 128.5, 128.1, 127.8, 126.7, 126.3, 125.9, 123.0, 96.7, 52.4, 39.2, 19.8. Anal. calcd for $C_{24}H_{23}NNiOS$: C 66.69, H 5.36, N 3.24; found C 67.17, H 5.24, N 3.00.

[(1*Z*,3*Z*)-3-(2-(Isopropylthio)ethylimino)-1,3-diphenylprop-1-en-1-olate]NiPh (2) Yield: 0.13 g (86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.72 (d, J=6.6 Hz, 2H), 7.58 (d, J=6.9 Hz, 2H), 7.44—7.20 (m, 8H), 7.02—6.90 (m, 3H), 5.72 (s, 1H, C=CH), 3.41—3.37 (m, 1H), 3.20—3.15 (m, 1H), 2.60—2.51 (m, 1H), 2.38 (t, J=6.3 Hz, 2H), 1.54 (d, J=5.1 Hz, 3H), 1.25 (d, J=4.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 172.0, 167.1, 148.8, 140.7, 139.1, 137.9, 129.1, 128.4, 128.0, 127.9, 126.7, 126.3, 125.6, 122.9, 96.6, 52.7, 39.3, 31.6, 21.8. Anal. calcd for $C_{26}H_{27}NNiOS$: C 67.85, H 5.91, N 3.04; found C 67.99, H 5.79, N 2.90.

[(1*Z*,3*Z*)-1,3-Diphenyl-3-(2-(propylthio)ethylimino)-prop-1-en-1-olate]NiPh (3) Yield: 0.40 g (87%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.70 (d, J=6.9 Hz, 2H), 7.55 (d, J=6.9 MHz, 2H), 7.43—7.20 (m, 8H), 7.02—6.92 (m, 3H), 5.72 (s, 1H, C=CH), 3.33—3.20 (m, 2H), 2.58—2.51 (m, 2H), 2.35—2.21 (m, 2H), 1.65—1.48 (m, 2H), 0.85 (t, J=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 172.2, 167.2, 148.8, 140.7, 139.2, 137.5, 129.1, 128.4, 128.1, 127.8, 126.7, 126.3, 125.7, 122.9, 96.6, 52.7, 38.2, 36.6, 21.6, 13.0. Anal. calcd for $C_{26}H_{27}NNiOS$: C 67.85, H 5.91, N 3.04; found C 67.95, H 6.09, N 2.93.

{(1*Z*,3*Z*)-3-[(2-(*tert*-Butylthio)ethylimino)-1,3-diphenylprop-1-en-1-olate}NiPh (4) Yield: 0.41 g (87%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.71 (d, J=6.6 Hz, 2H), 7.58 (d, J=6.9 Hz, 2H), 7.43—7.22 (m, 8H), 6.99—6.87 (m, 3H), 5.71 (s, 1H, C=CH), 3.27 (br s, 2H), 2.43 (br s, 2H), 1.25 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.9, 167.1, 147.3, 140.8, 139.1, 138.8, 129.0, 128.4, 128.0, 127.8, 126.7, 126.3, 125.3, 122.9, 96.5, 53.0, 50.1, 34.5, 30.0. Anal. calcd for $C_{27}H_{29}NNiOS$: C 68.37, H 6.16, N 2.95; found C 68.49, H 6.32, N 2.96.

[(1*Z*,3*Z*)-1,3-Diphenyl-3-(2-(phenylthio)ethylimino)prop-1-en-1-olate]NiPh (5) Yield: 0.41 g (83%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.41—8.38 (m, 2H), 7.73 (d, J=6.6 Hz, 2H), 7.49—7.21 (m, 13H), 6.94—6.82 (m, 3H), 5.79 (s, 1H, C=CH), 3.25—3.16 (m, 1H), 3.15—3.09 (m, 1H), 3.03—2.83 (m, 1H), 2.48—2.40 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 172.2, 167.5, 146.4, 140.8, 139.0, 137.7, 133.8, 130.0, 129.6, 129.4, 129.2, 128.5, 128.1, 127.9, 126.8, 126.3, 125.6, 123.0, 96.8, 51.9, 43.2. Anal. calcd for $C_{29}H_{25}NNiOS$: C 70.47, H 5.10, N 2.83; found C 70.58, H 4.81, N 2.42.

[(1*Z*,3*Z*)-3-(2-(Cyclohexylthio)ethylimino)-1,3-diphenylprop-1-en-1-olate]NiPh (6) Yield: 0.23 g (91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.71 (d, J=6.6 Hz, 2H), 7.56 (d, J=6.9 Hz, 2H), 7.44—7.19 (m, 8H), 7.00—6.89 (m, 3H), 5.71 (s, 1H, C=CH), 3.32—3.25 (m, 1H), 3.25—3.16 (m, 1H), 2.73—2.68 (m, 1H), 2.39 (t, J=6.6 Hz, 2H), 2.31—2.23 (m, 1H), 2.05—1.98 (m, 1H), 1.74—1.70 (m, 2H), 1.76—1.50 (m, 1H), 1.50—1.31 (m, 2H), 1.31—1.00 (m, 3H); ^{13}C NMR (75 Hz, $CDCl_3$) δ: 172.0, 167.1, 148.5, 140.8, 139.2, 138.0, 129.0, 128.4, 128.0, 127.8, 126.7, 126.4, 125.5, 122.8, 96.6, 52.9, 47.3, 32.4, 32.1, 26.4, 25.1. Anal. calcd for $C_{29}H_{31}NNiOS$: C 69.62, H 6.25, N 2.80; found C 69.66, H 6.19, N 2.48.

[(1*Z*,3*E*)-3-(2-(Isopropylthio)ethylimino)-1-phenylbut-1-en-1-olate]NiPh (7) Yield: 0.59 g (94%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.71 (dd, J=2.1, 7.8 Hz, 2H), 7.52 (d, J=6.6 Hz, 2H), 7.28—7.21 (m, 3H), 6.98—6.87 (m, 3H), 5.69 (s, 1H, C=CH), 3.59—3.57 (m, 1H), 3.30—3.47 (m, 1H), 2.62—2.52 (m, 3H), 2.03 (s, 3H), 1.50 (br s, 3H), 1.26 (br s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.5, 165.1, 148.8, 139.3, 137.9, 128.8, 127.8, 126.6, 125.4, 122.7, 96.5, 50.7, 39.0, 31.7, 23.4, 21.7. Anal. calcd for $C_{21}H_{25}NNiOS$: C 63.34, H 6.33, N 3.52; found C 63.76, H 6.48, N 3.74.

[(2*Z*,4*Z*)-5,5,5-Trifluoro-4-(2-(isopropylthio)ethylimino)pent-2-en-2-olate]NiPh (8) Yield: 0.63 g (90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.38—7.32 (m, 2H), 6.90—6.86 (m, 3H), 5.42 (s, 1H, C=CH), 3.62—3.54 (m, 1H), 3.30—3.24 (m, 1H), 2.53—2.46 (m, 3H), 1.99 (s, 3H), 1.60—1.40 (m, 3H), 1.40—1.25 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.3, 161.0, 160.6, 160.2, 159.8, 145.1, 137.6, 125.6, 124.8, 123.2, 121.0, 117.3, 113.5, 96.3(4), 96.3(1), 51.0, 39.5, 31.1, 23.1, 21.7; ^{19}F NMR (282 MHz, $CDCl_3$) δ: −73.5. Anal. calcd for $C_{16}H_{20}F_3NNiOS$: C 49.26, H 5.17, N 3.59, found C 49.70, H 5.42, N 3.59.

[(1*Z*,3*Z*)-3-(2-(Dimethylamino)ethylimino)-1,3-diphenylprop-1-en-1-olate]NiPh (9) Yield: 0.18 g (86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.87 (d, J=7.2 Hz, 2H), 7.42—6.88 (m, 13H), 5.69 (s, 1H, C=CH), 3.10 (t, J=6.0 Hz, 2H), 3.35 (s, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 172.1, 166.4, 159.3, 140.0, 139.1, 135.9, 128.7, 128.4, 128.2, 127.7, 126.5, 126.4, 124.9, 121.9, 96.5, 65.2, 49.8, 49.2. Anal. calcd for $C_{25}H_{26}N_2NiO$: C 69.96, H 6.11, N 6.53; found C 69.51, H 6.03, N 6.50.

[(1*Z*,3*Z*)-3-(2-(Diphenylphosphino)ethylimino)-1,3-diphenylprop-1-en-1-olate]NiPh (10) Yield: 0.23 g (89%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.71 (d, J=6.9 Hz, 2H), 7.59—7.18 (m, 20H), 6.77—6.75 (m, 3H), 5.81 (s, 1H, C=CH), 3.29 (t, J=6.3 Hz, 1H), 3.21 (t, J=6.3 Hz, 1H), 2.21—2.14 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 172.2, 167.8, 152.6, 151.9, 141.6, 139.8(3) 139.7(7), 138.0(3), 138.0(0), 133.3, 133.2, 130.6, 130.5(7), 130.3, 129.7, 129.0, 128.5, 128.4, 128.3, 127.8(4), 127.8(2), 126.9, 126.5, 125.5(3), 125.5(1), 122.0, 96.7, 51.4(4), 51.3(7), 32.2, 31.9; ^{31}P NMR (121 MHz, $CDCl_3$) δ: 48.53. Anal. calcd for $C_{35}H_{30}NNiOP$:

C 73.71, H 5.30, N 2.46; found C 73.87, H 5.17, N 2.26.

[(1*Z*,3*Z*)-3-(2-Phenoxyethylimino)-1,3-diphenylprop-1-en-1-olate]NiPh(PPh$_3$) (11) Yield: 0.53 g (92%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.60—7.54 (m, 7H), 7.35—7.08 (m, 17H), 6.91—6.71 (m, 8H), 6.53—6.49 (m, 3H), 5.71 (s, 1H, C=CH), 4.12 (t, J=6.3 Hz, 2H), 2.94 (t, J=2.9 Hz, 2H); ^{13}C NMR (75 MHz, C_6D_6) δ: 171.6, 170.4, 159.8, 152.7, 152.1, 142.5(2), 142.4(7), 139.3, 138.5, 134.9, 134.7, 132.3, 131.7, 129.8, 129.5, 129.0, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7(7), 127.68, 126.8, 126.5, 122.2, 120.5, 115.2, 98.6, 70.7, 53.5; ^{31}P NMR (121 MHz, $CDCl_3$) δ: 29.00. Anal. calcd for $C_{47}H_{40}NNiO_2P$: C 76.23, H 5.44, N 1.89; found C 76.48, H 5.41, N 1.93.

[(1*Z*,3*Z*)-1,3-Diphenyl-3-(pyridin-2-ylmethylimino)prop-1-en-1-olate]NiPh (12) Yield: 0.25 g (81%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.83—6.84 (m, 19H), 5.84 (s, 1H, C=CH), 4.54 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 172.9, 166.6, 164.0, 159.9, 152.7, 139.6, 139.0, 136.8, 136.2, 129.1, 128.8, 128.4, 127.9, 126.6, 126.2, 125.6, 122.7, 122.5, 119.5, 96.9, 59.4. Anal. calcd for $C_{27}H_{22}N_2NiO$: C 72.20, H 4.94, N 6.24; found C 71.67, H 5.28, N 6.02.

(1*Z*,3*E*)-3-[2-(2,6-Dimethylphenylthio)phenylimino)-1-phenylbut-1-en-1-olate]NiPh(PPh$_3$) (13) Yield: 0.20 g (74%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.61—7.58 (m, 6H), 7.40—7.09 (m, 14H), 7.00—6.91 (m, 4H), 6.46 (t, J=7.5 Hz, 1H), 6.31—6.16 (m, 4H), 6.05 (d, J=7.2 Hz, 1H), 5.94 (d, J=6.9 Hz, 1H), 5.97 (s, 1H, C=CH), 5.77 (t, J=7.2 Hz, 1H), 2.52 (s, 6H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.4, 167.4, 151.6, 151.1, 148.4, 144.6, 139.1, 138.5, 135.3, 134.5, 134.4, 132.2, 131.9, 131.5, 130.3, 129.4, 129.1, 129.0, 128.7, 128.4, 128.2, 127.7, 127.6, 127.4, 127.2, 126.3, 125.4, 123.9, 123.5, 123.3, 121.9, 120.3, 95.6, 24.8(1), 24.7(8), 22.0; ^{31}P NMR (121 MHz, $CDCl_3$) δ: 28.8. Anal. calcd for $C_{48}H_{42}NNiOPS$: C 74.82, H 5.49, N 1.82; found C 74.42, H 5.68, N 1.48.

{(1*Z*,3*E*)-1-Phenyl-3-[2-(phenylthio)phenylimino]-but-1-en-1-olate}NiPh(PPh$_3$) (14) Yield: 0.62 g (82%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.62—7.56 (m, 8H), 7.35—7.10 (m, 14H), 6.96—6.87 (m, 4H), 6.60—6.53 (m, 2H), 6.45—6.42 (m, 2H), 6.26—6.19 (m, 2H), 6.08—6.06 (m, 1H), 5.89—5.86 (m, 2H), 1.70 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.5(0), 171.4(8), 166.9, 151.4, 150.8, 149.2, 139.1, 138.3(0), 138.2(9), 136.1, 136.0, 134.5(0), 134.4(6), 134.3, 133.5, 132.9, 131.9, 131.3, 129.3(8), 129.3(5), 129.2, 128.7, 128.0, 127.7, 127.6, 127.3, 126.3, 126.1, 125.7, 125.2(9), 125.2(6), 124.6, 124.1, 124.0, 123.5, 120.3(4), 120.3(1), 95.6, 25.1, 25.0; ^{31}P NMR (121 MHz, $CDCl_3$) δ: 28.9. Anal. calcd for $C_{46}H_{38}NNiOPS$: C 74.41, H 5.16, N 1.89; found C 74.50, H 5.25, N 1.83.

General procedure for ethylene dimerization

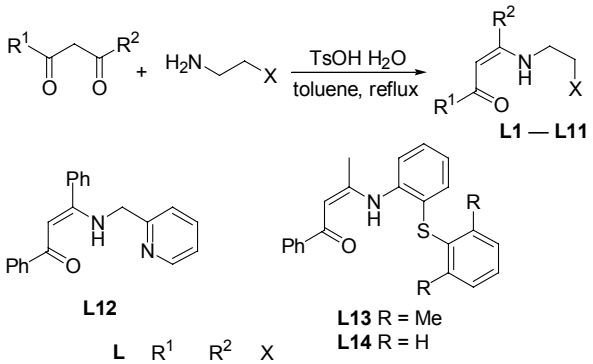
To a dry 300 mL stainless-steel autoclave was charged with dichloromethane (100 mL). Then the desired amount of cocatalyst and the solution of catalyst in dichloromethane (1 mL) was introduced into the reactor under nitrogen. After stirring for 10 min at desired temperature, ethylene was continuously fed to maintain the ethylene pressure at desired pressure for 5 or 10 min. Then acidified EtOH and heptane (as internal standard) was injected at −78 ℃ to quench the reaction. Quantitative GC analysis of the product was performed immediately after the termination of the reaction.

Results and Discussion

Synthesis and characterization of the Ni(II) complexes

The ligands were readily available in moderate to good yields by a known procedure (Scheme 1).[14e-14g] The structures were well-characterized by ^{1}H, ^{13}C NMR, MS, elemental analysis, and IR spectra. A signal at around δ 188 in the ^{13}C NMR spectra of the ligands displays the C=O group in β-carbonylenamines.

Scheme 1 Synthesis of the ligands **L1—14**



L	R^1	R^2	X
1	Ph	Ph	SMe
2	Ph	Ph	SPr-*i*
3	Ph	Ph	SPr-*n*
4	Ph	Ph	SBu-*t*
5	Ph	Ph	SPh
6	Ph	Ph	SCy
7	Ph	CH_3	SPr-*i*
8	CH_3	CF_3	SPr-*i*
9	Ph	Ph	NMe_2
10	Ph	Ph	PPh_2
11	Ph	Ph	OPh

Initially, we tried to prepare the corresponding nickel complexes by slowly adding the lithium salts of ligands in toluene to the suspension of NiPhCl(PPh$_3$)$_2$ in dry toluene, but failed to obtain the corresponding complexes. To our delight, when we modified the procedure by mixing the lithium salt of **L1—L14** with NiPhCl(PPh$_3$)$_2$ first, followed by adding toluene at −30 ℃, complexes **1—14** were obtain as air- and moisture-sensitive solids in good yields (Scheme 2). **1—14** are easily soluble in toluene, dichloromethane, and tetrahydrofuran at room temperature and the structures of **1—14** were well-characterized by ^{1}H, ^{13}C, ^{31}P NMR, and elemental analysis. Similar to the corresponding titanium complexes,[14f-14g] ^{13}C NMR analysis of complexes **1—14** showed that the chemical shift higher than

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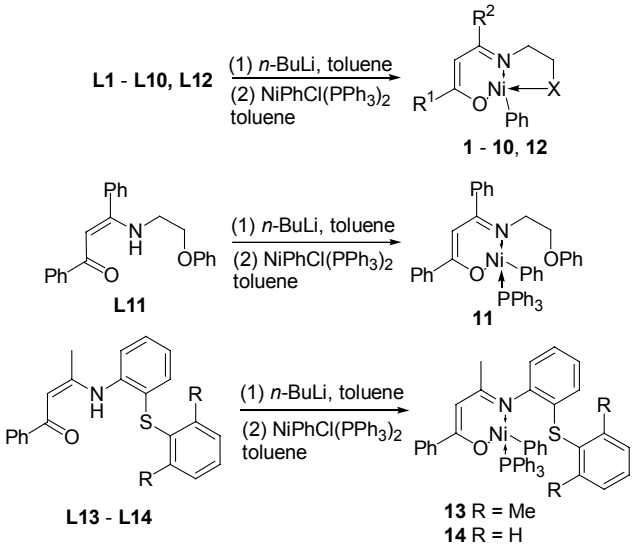
δ 180 (carbonyl group in the ligands) disappeared and two signals at around δ 170 were observed. This observation is confirmed by the X-ray analysis. As shown in Figure 1, X-ray crystallographic analysis of **7** reveals that the ligand coordinats nickel atom with oxygen, nitrogen, and sulfur atoms. The geometry around nickel adopts a distorted square planar. The phenyl group attached to Ni lies *trans* to N(1) with an N(1)-Ni(1)-C(20) angle of 176.73(13)°. The O(1), N(1), S(1), and C(20) atoms are nearly coplanar, with O(l) and S(1) occupying the *trans* position [O(l)-Ni(1)-S(1): 174.91(8)º, N(1)-Ni(1)-C(20): 176.73(13)º]. The Ni(1)—N(1) bond length is 1.932(2) Å. The bond length of O(1)—Ni(1) (1.863(2) Å) is shorter than that of the reported salicylaldiminato nickel(II) complex (O—Ni 1.910(3) Å).[16] The O(1)—C(9) is lengthened and N(1)—C(7) is shortened as compared to the corresponding ligand.[14f] It is worthy to note that a strong coordination effect exists between sulfur and nickel, as the Ni(1)—S(1) bond length is 2.1389(10) Å (the sum of Van der Waals radius is 4.37 Å). For each complex, satisfactory elemental analyses were obtained. Together with both ^{1}H NMR and ^{13}C NMR spectroscopy analysis, it is deduced that the molecular structures of complexes **1**—**6**, **8**—**10** and **12** are similar to that of **7**.

Scheme 2 Synthesis of nickel(II) complexes



To our surprise, signals above δ 20.0 in the ^{31}P NMR spectra were observed in the case of complexes **11, 13,** and **14**, which are assigned as the signals for the triphenylphosphine coordinated to metal. X-ray analysis of both **13** and **14** confirmed the molecular structure (Figures 2 and 3). As showed in Figure 2, **L13** acts as a bidentate ligand, and a PPh_3 coordinated to the metal. The O(1), N(1), P(1), and C(25) atoms constitute a distorted square planar geometry around nickel(II), with O(l) and C(25) occupying the *trans* position [O(l)-Ni(1)-C(25): 168.67(15)º, N(1)-Ni(1)-P(1): 178.83(10)º]. The bond length of both O(1)—Ni(1)

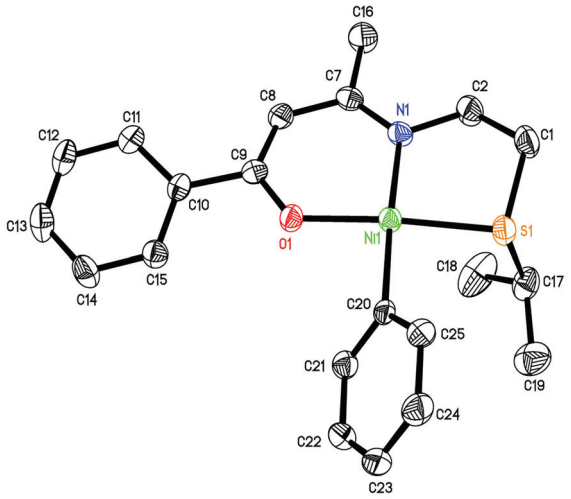


Figure 1 Molecular structure of **7**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (º): Ni(1)—O(1) = 1.863(2), Ni(1) — N(1) = 1.932(2), Ni(1) — S(1) = 2.1389(9), Ni(1) — C(20) = 1.914(3), C(7) — C(8) = 1.413(5), C(8)—C(9) = 1.369(5), O(1)—C(9) = 1.293(4), N(1)—C(7) = 1.308(4), O(1)-Ni(1)-C(20) = 87.55(11), O(1)-Ni(1)-N(1) = 95.34(11), C(20)-Ni(1)-N(1) = 176.73(13), O(1)-Ni(1)-S(1) = 174.91(8), C(20)-Ni(1)-S(1) = 87.37(9), N(1)-Ni(1)-S(1) = 89.74(9), C(1)-S(1)-C(17) = 104.7(2), C(1)-S(1)-Ni(1) = 99.14(12), C(17)-S(1)-Ni(1) = 108.37(13).

(1.905(2) Å) and Ni(1)—N(1) (1.926(3) Å) are longer than that of **7**. The O(1)—C(9) bond (1.272(4) Å) is shorter than that of complex **7**, and N(1)—C(7) (1.319(5) Å) is longer than that of complex **7**. The distances between S and Ni atoms in **13** and **14** (3.363 & 3.458 Å, respectively) mean that the corresponding SAr groups coordinate with the metal weakly.

Ethylene dimerization

In the presence of MAO, complex **2** was selected to screen the ethylene oligomerization under different conditions (Table 2). To our delight, the ethylene was dimerized in very high activity [1.20×10^{6} g/(mol(Ni)•h•atm)] at 0 ℃ and 10 atm ethylene atmosphere along with good selectivity towards 1-butene (84.2%). A even higher activity [1.91×10^{6} g/(mol(Ni)•h•atm)] was observed when prolonging the reaction time (Table 2, Entry 7). We suppose that the violent exothermic reaction, which resulted in the rapid rise of the system temperature, induced rapid isomerization of the formed butene. When the ethylene dimerization was carried out at 10 atm ethylene pressures, reducing the reaction temperature from 0 to −15 ℃ resulted in the selectivity increase of 1-butene from 84.2% to 90.2% (Table 2, Entries 1 vs. 2), and the 1-butene selectivity reached to above 99% when the reaction temperature was further reduced to −78 ℃ (Table 2, Entry 5). As a result, the lower the temperature, the better the 1-butene selectivity. However, the activity was sharply reduced to 0.01×10^{6}

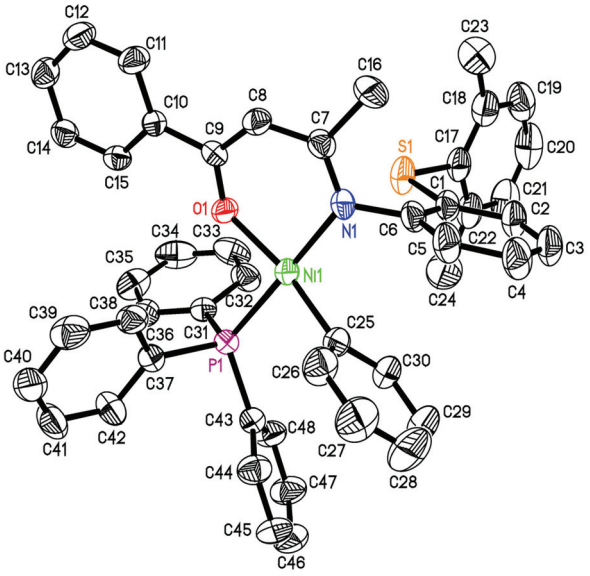


Figure 2 Molecular structure of **13**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ni(1)—C(25) = 1.880(4), Ni(1)—O(1) = 1.905(2), Ni(1)—N(1) = 1.926(3), Ni(1)—P(1) = 2.1713(11), O(1)—C(9) = 1.272(4), C(7)—C(8) = 1.406(5), C(8)—C(9) = 1.362(5), N(1)—C(7) = 1.319(5), C(25)-Ni(1)-O(1) = 168.67(15), C(25)-Ni(1)-N(1) = 93.40(15), O(1)-Ni(1)-N(1) = 92.15(11), C(25)-Ni(1)-P(1) = 88.31(12), O(1)-Ni(1)-P(1) = 86.40(8), N(1)-Ni(1)-P(1) = 178.83(10).

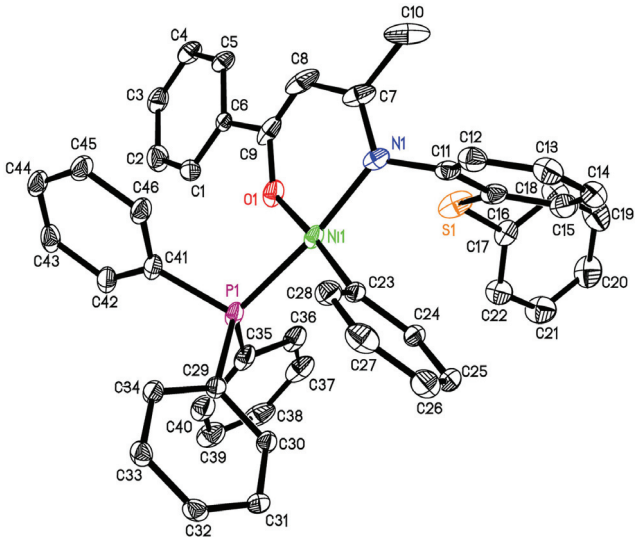


Figure 3 Molecular structure of **14**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni(1)—O(1) = 1.9089(16), Ni(1)—N(1) = 1.924(2), Ni(1)—C(23) = 1.886(2), Ni(1)—P(1) = 2.1667(7), O(1)—C(9) = 1.279(3), N(1)—C(7) = 1.324(3), C(7)—C(8) = 1.409(4), C(8)—C(9) = 1.387(5), N(1)-Ni(1)-P(1) = 172.77(6), C(23)-Ni(1)-O(1) = 174.57(9), C(23)-Ni(1)-N(1) = 93.29(9), O(1)-Ni(1)-N(1) = 91.60(8), C(23)-Ni(1)-P(1) = 89.83(7), O(1)-Ni(1)-P(1) = 85.59(6).

Table 1 Crystal data and summary of data collection and refinement details for **7**, **13**, and **14**

Complex	**7**	**13**	**14**
Empirical formula	$C_{21}H_{25}NNiOS$	$C_{48}H_{42}NNiOPS$	$C_{46}H_{38}NNiOPS$
Formula weight	398.19	770.57	742.51
Temperature/K	293(2)	293(2)	133(2)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	$P2_1$	P-1	P-1
a/Å	10.0376(19)	9.8968(6)	10.7669(12)
b/Å	11.540(2)	14.0467(9)	11.6150(12)
c/Å	16.583(3)	18.2858(12)	16.1448(17)
α/(°)	90	103.4080(10)	106.895(2)
β/(°)	90	101.9770(10)	90.086(2)
γ/(°)	90	101.289(2)	107.532(2)
V/Å^3	1920.8(6)	2338.1(3)	1833.4(3)
Z	4	2	2
D_c/(Mg•m^{-3})	1.377	1.095	1.345
Size/mm	0.285×0.226×0.135	0.307×0.269×0.211	0.35×0.32×0.20
Limiting indices	$-12\leqslant h\leqslant 12$, $-11\leqslant k\leqslant 14$, $-20\leqslant l\leqslant 19$	$-11\leqslant h\leqslant 11$, $-17\leqslant k\leqslant 16$, $0\leqslant l\leqslant 22$	$-13\leqslant h\leqslant 13$ $-14\leqslant k\leqslant 14$ $-20\leqslant l\leqslant 20$
Absorption coefficient/mm^{-1}	1.127	0.525	0.667
F(000)	840	808	776

Continued

Complex	**7**	**13**	**14**
θ range for data collection/(°)	2.15 to 26.00	1.54 to 25.50	1.32 to 27.00
Reflections collected/unique	10376/3738 [R(int)＝0.0340]	8549/8549 [R(int)＝0.0000]	13435/7892 [R(int)＝0.0215]
Absorption correction	Empirical	Empirical	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.70928	1.0000 and 0.0968	0.8781 and 0.8000
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3738/0/229	8549/0/481	7892/*1*/520
Goodness-of-fit on F^2	1.039	0.898	0.951
Final R indices [$I > 2\sigma(I)$]	R_1＝0.0396, wR_2＝0.0785	R_1＝0.0598, wR_2＝0.1235	R_1＝0.0395, wR_2＝0.1178
R indices (all data)	R_1＝0.0468, wR_2＝0.0813	R_1＝0.1221, wR_2＝0.1412	R_1＝0.0510, wR_2＝0.1314
Largest diff. peak and hole/(e•Å^{-3})	0.458 and −0.201	0.379 and −0.267	0.318 and −1.084

g/(mol(Ni)•h•atm) when ethylene was dimerized at −78 ℃. Corresponding to it, the activity was improved to 7.54×10^6 g/(mol(Ni)•h•atm) with the selectivity of 1-butene being only 59.9% when the ethylene dimerization was processed at 40 ℃. Decreasing in selectivity with the rise of temperature is consistent with the rapid β-H elimination and reinsertion to Ni—H at higher temperature. The rapid β-H elimination and reinsertion to Ni—H could also be observed from the fact that the selectivity of 1-butene reduces to 70.8% when the polymerization proceeds for 10 min (Table 2, Entry 7). High pressure favors the formation of 1-butene. For example, butene was obtained in an activity of 1.05×10^6 g/(mol(Ni)•h•atm) with 93.9% selectivity toward 1-butene at 15 atm and −15 ℃ (Table 2, Entry 3). 2000 is a preferred Al/Ni ratio as too low Al/Ni ratio (500) resulted in both a reduced activity and a low 1-butene selectivity (Table 2, Entry 8). The 1-butene selectivity could be improved to 86.1% when Al/Ni ratio reaches 3000, while the activity was slightly deteriorated (Table 2, Entry 9). Et_2AlCl also was a good cocatalyst (Table 2, Entry 12). While activation **2** with 1000 equivalent of Et_3Al produced an unfavorable catalyst system (Table 2, Entry 13).

In the presence of MAO, all complexes have been found to be active in catalyzing the ethylene dimerization into butene with excellent selectivity, and in all cases no polymer was observed. The structures of the complexes influence both the activity and selectivity significantly (Table 3). For most of the catalysts bearing a thioether as a sidearm, the activities are above 1×10^6 g/(mol(Ni)•h•atm) (Table 3, Entries 1—7). In the cases of R^2 being electron-withdrawing CF_3, the activity decreased to 0.35×10^6 g/(mol(Ni)•h•atm) (Table 3, Entry 8). Employing PPh_2 as a sidearm group, the activity reached 3.16×10^6 g/(mol(Ni)•h•atm) (Table 3, Entry

Table 2 Ethylene dimerization in the presence of **2**[a]

Entry	Cocatalyst	Al∶Ni	Temp./℃	Time/min	p/atm	Activity[b]	Selectivity[c]/%	
							Butene	1-Butene
1	MAO	1000	0	5	10	1.20	＞99	84.2
2	MAO	1000	−15	5	10	1.05	＞99	90.2
3	MAO	1000	−15	5	15	1.05	＞99	93.9
4	MAO	1000	−60	5	15	0.08	＞99	96.0
5	MAO	1000	−78	5	15	0.01	＞99	＞99
6	MAO	1000	0	5	5	0.20	＞99	80. 8
7	MAO	1000	0	10	10	1.91	＞99	70.8
8	MAO	500	0	5	10	0.21	＞99	78.3
9	MAO	2000	0	5	10	1.91	＞99	84.0
10	MAO	3000	0	5	10	1.45	＞99	86.1
11	MAO	1000	40	5	10	7.54	85.7[d]	59.9
12	Et_2AlCl	1000	0	5	10	1.08	＞99	81.8
13	Et_3Al	1000	0	5	10	0.05	＞99	70.9

[a] Catalyst (0.46 mg, 1 μmol), MAO (1.5 mol/L in toluene), 100 mL CH_2Cl_2. [b] In unit of 10^6 g/(mol(Ni)•h•atm). [c] Determined by GC and GC-MS. [d] Hexenes were observed.

Table 3 Some Results for Ethylene Dimerization catalyzed by Complexes **1**—**14**

Entry[a]	Complex	Activity [10^6 g/(mol(Ni)•atm•h)]	Selectivity[b,c]/%	
			Butene	1-Butene
1	**1**	1.84	95.68	81.26
2	**2**	1.20	>99	84.17
3	**3**	5.20	98.44	65.70
4	**4**	3.14	>99	82.25
5	**5**	2.63	>99	74.77
6	**6**	1.18	>99	86.58
7	**7**	2.27	94.05	77.03
8	**8**	0.35	>99	87.68
9	**9**	0.91	>99	87.02
10	**10**	3.16	97.18	18.89
11	**11**	9.35	90.87	12.63
12	**12**	1.03	>99	85.29
13	**13**	8.44	89.77	10.12
14	**14**	4.68	90.93	11.14
15[d]	**2**	14.25	89.65	15.89

[a] 1 μmol of catalyst, MAO (1 mmol, 1.5 mol/L in heptane), Al∶Ni=1000, 100 mL CH_2Cl_2, 5 min, 0 ℃, 10 atm. [b] Determined by GC and GC-MS. [c] Hexene and octene were also observed. [d] 1 μmol of Ph_3P was added.

10). For pyridine-containing complex **12**, an activity of 1.03×10^6 g/mol$_{Ni}$•atm•h was achieved. Complexes **11, 13** and **14** gave excellent activities [up to 9.35×10^6 g/(mol(Ni)•h•atm)]. However, in these cases, the selectivities of 1-butene were only about 10%. When complex **2** was employed in the presence of one equivalent of Ph_3P, the oligomerization activity was improved to 14.25×10^6 g/(mol(Ni)•h•atm), and correspondingly, the selectivity for 1-butene reduced to 15.89%.

Conclusions

A series of *β*-ketoimine-derived nickel(II) complexes have been synthesized and characterized. X-ray analysis proved that the structures of the complexes deeply depend on the properties of the pendant coordination group. In the presence of MAO, these nickel(II) complexes showed very high activity [up to 14.25×10^6 g/(mol(Ni)•h•atm)] toward ethylene dimerization. Good selectivity for 1-butene is also obtained when the pendant groups coordinate to nickel. Under the optimal conditions, the selectivity towards 1-butene reaches to above 99%. Further studies on the mechanism are under investigation in our laboratory.

Acknowledgement

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