

Activation of Single-Component Nickel(II) Polyethylene Catalysts via Phase Transfer of Fluorous Phosphine Ligands

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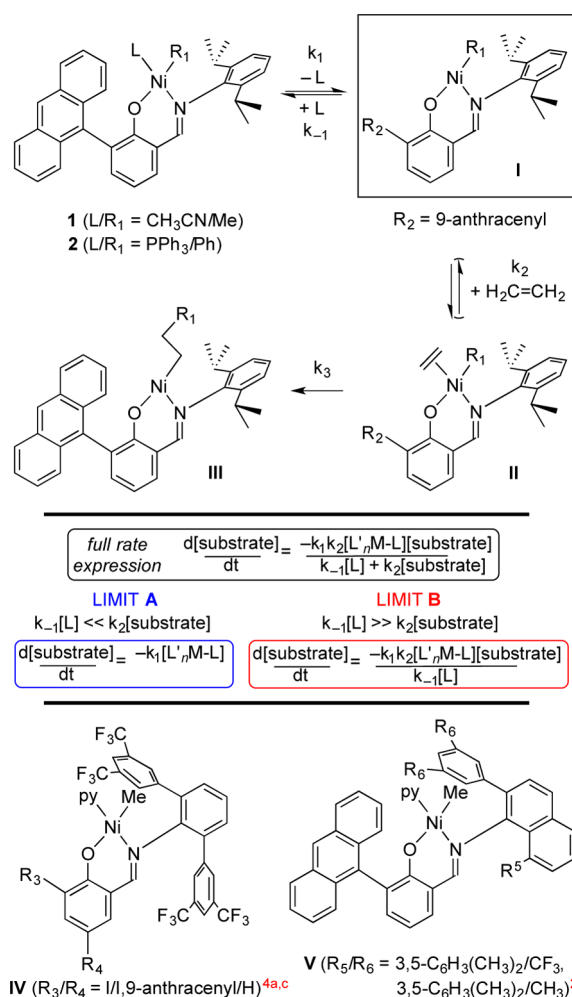
S Supporting Information

ABSTRACT: The nickel salicylaldiminato phosphine complexes [1,2,3-C₆H₃(9-anthracenyl)O(CH=N(2,6-C₆H₃(iPr)₂)]Ni(Me)[P(4-C₆H₄R)₃] (**4**; R = **a**, (CH₂)₂R₁₈; **b**, (CH₂)₃R₁₈; **c**, H (R₁₈ = (CF₂)₇CF₃)) are prepared from the corresponding phosphines **3a–c** and nickel NCMe adduct (46–68%). These are applied as catalysts for ethylene polymerization in toluene and fluorous/toluene liquid/liquid biphasic mixtures. Under the latter conditions, the fluorous phosphines **3a,b** that must dissociate to generate the active catalyst migrate to the fluorous phase (partition coefficients 97.5:2.5 and 66.6:33.4 vs <0.5:>99.5 for **4a,b**). Catalysts **4a,b** show marked accelerations under biphasic conditions, but **4c** (which has a lipophilic phosphine ligand) does not. Under all conditions, **4a,b** are faster catalysts than the Ni(Ph)₂(PPh₃) analogue, a previously reported benchmark.

Over the past 15 years, the development of single-component square planar nickel(II) catalysts for the polymerization of ethylene has received intense attention.^{1–5} One impetus has been the compatibility of such late transition metal catalysts, which are distinguished by their moderated electrophilicity, with polar monomers that contain carboxylic acid or alcohol derivatives, and the ability to attain heretofore inaccessible copolymers. As depicted in Scheme 1, many of these incorporate salicylaldiminato ligands (**1** and **2** or **IV** and **V**),^{1,2c,4,5b} although other types of C–O/C=NAr or C=O/C–NAr chelates have been employed.^{2a,b,5a,c} The ligating C–O moieties in **1** and **2** feature bulky *ortho* substituents to inhibit the formation of bis(salicylaldiminato) complexes. The *N*-aryl groups contain two bulky *ortho* substituents, the purpose of which is to sterically shield sites axial to the nickel coordination plane, thereby inhibiting the rate of chain transfer relative to propagation. These properties have allowed a variety of microstructures to be engineered into high-molecular-weight polymers.

High turnover frequencies (TOFs) are more challenging to achieve with neutral single-component polyethylene catalysts as opposed to multi-component systems where an activator aids the abstraction of a ligand. The latter are exemplified by MAO and early transition metal halides, which deliver highly electrophilic cationic species, as well as many earlier generation nickel catalysts.^{1a} We have sought to develop a protocol termed “phase-transfer catalyst activation”, whereby a ligand in a catalyst precursor that must dissociate to generate the active

Scheme 1. Mechanism of Ethylene Polymerization by Nickel Salicylaldiminato Catalysts **1 and **2**, Rate Expressions, and Other Representative Catalysts (**IV** and **V**)**



catalyst is phase labeled, such that it rapidly transfers to a second phase orthogonal to the catalyst and reactants.^{6–8} Rate accelerations can be expected when the initial dissociation is reversible, and the substrate and ligand compete for the active catalyst ($k_{-1}[L] \geq k_2[\text{substrate}]$), as depicted with intermediate

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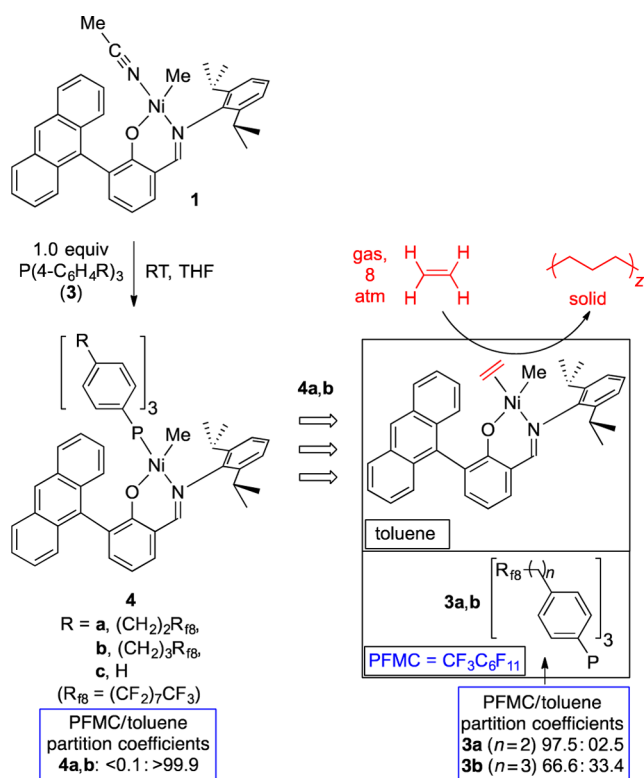
I in Scheme 1. When the former term dominates in the full rate expression (Scheme 1), the limit B obtains, and anything that diminishes the ligand concentration ($[L]$) will increase the reaction velocity. Furthermore, in the case of polymerizations, the ligand can potentially inhibit every propagation cycle (e.g., addition of L as opposed to ethylene to III in Scheme 1).

Studies with catalyst 2 and related species have established that, under the usual ethylene pressures, re-addition of the dissociated ligand PPh_3 to the intermediate I is faster than the subsequent binding of ethylene.^{1a} Thus, these seemed to provide ideal testing grounds for our phase-transfer activation methodology, which has so far been applied to fluoros/organic and aqueous/organic liquid/liquid biphasic systems, as well as liquid/solid biphasic systems,^{6–8} but has not yet been generalized beyond olefin metathesis with ruthenium catalysts.

Fluorous/organic liquid/liquid or solid/liquid biphasic systems have been extensively applied in catalysis over the past 20 years,⁹ and one consequence is the ready synthetic and/or commercial availability of fluoros phosphines. Thus, we sought variants of 1 or 2 that would remain lipophilic, such that the catalyst precursor would not significantly leach into a fluoros phase but contained a fluorophilic triarylphosphine. As shown in Scheme 2, 1 was treated with $\text{P}(4\text{-C}_6\text{H}_4\text{R})_3$ (3),¹⁰ in which the fluoros *para* substituents (R = a, $(\text{CH}_2)_2\text{R}_{18}$; b, $(\text{CH}_2)_3\text{R}_{18}$; $\text{R}_{18} = (\text{CF}_2)_7\text{CF}_3$) differ in the number of insulating methylene “spacers”. For control purposes, the parent non-fluorous phosphine PPh_3 (3c) was also employed.

Workups gave the expected nickel(II) complexes 4a–c (Scheme 2) as orange powders in 46–68% yields. These were soluble in most common organic solvents and characterized by NMR as described in the Supporting Information (SI). All

Scheme 2. Syntheses of New Ethylene Polymerization Catalysts, and Biphasic Fluorous/Organic Reaction Conditions



features were routine. Partition coefficients were measured by NMR using mixtures of perfluoro(methylcyclohexane) (PFMC) and toluene, and showed 4a,b to be highly lipophilic (concentration ratios <0.5:>99.5; see SI). The analogous partition coefficient of the phosphine 3a was found to be 97.5:2.5;¹¹ that of 3b, 66.6:33.4, had been reported previously.^{10a} Earlier studies have bound the perfluoro-hexanes/pentane partition coefficient of PPh_3 as <0.5:>99.5.¹² The shorter methylene spacer in 3a should—besides enhancing fluorophilicity—render it a better leaving group and poorer nucleophile than 3b (faster k_1 and slower k_{-1} in Scheme 1).

Polymerizations were conducted at room temperature under 100 psig of ethylene (8 atm) as detailed in the SI. In all cases, ca. 10 mg of catalyst and 10.0 mL of toluene were employed, together in some cases with 5.0 mL of a fluoros solvent. Rates were assayed by the ethylene uptake needed to maintain constant pressure, and the TOF values were expressed as grams of polyethylene (adsorbed ethylene) per mole of catalyst per hour. After 60 min, workups gave polyethylene as a white solid, which was characterized as summarized in Table 1.

Figure 1A compares the rate profiles for polymerizations catalyzed by 4a in toluene (10.0 mL, blue diamonds) and a toluene/PFMC biphasic mixture (10.0/5.0 mL, red squares). As can be seen, the biphasic polymerization was distinctly faster. Since fluoros solvents commonly exhibit higher solubilities than organic solvents for nonpolar diatomic gases such as O_2 , H_2 , and N_2 ,¹³ it was of interest to check for any unanticipated effects with ethylene as a possible factor in the rate trend. However, the solubility of ethylene proved greater in toluene than PFMC (30 vs 20 g/L under 8 atm), as assayed by a standard procedure (see SI).

Next, analogous monophasic and biphasic polymerizations were conducted using the catalyst with the less fluoros phosphine ligand, 4b. As shown in Figure 1B, a distinct rate acceleration was again obvious (blue diamonds vs red squares), but less dramatic than with 4a in Figure 1A. This is consistent with the lower fluorophilicity and less biased partition coefficient of the phosphine 3b vs 3a. It is furthermore in accord with the higher nucleophilicity noted above, which would decrease the k_2/k_{-1} ratio.

Returning to Figure 1A, a second biphasic polymerization was carried out, but using perfluoro(2-butyltetrahydrofuran) (FC-75) as the fluoros solvent (green triangles). The rate was again accelerated versus the monophasic experiment, but to a lesser extent, and this diminished with time. In other catalytic reactions, FC-75 has given faster rates than PFMC.^{6a,b} The basis for the influence of fluoros solvents upon rates, and the weak inflection points apparent after 10 min when polymerizations are conducted with 4a,b in toluene/PFMC (Figure 1), remain under investigation.

In response to a reviewer’s suggestion, the polymerizations in toluene and toluene/PFMC in Figure 1A were repeated under 42 psig of ethylene (ca. 4 atm). As shown in Figure s2, both were slower, consistent with an enhanced competitiveness of the k_{-1} vs k_2 step, but the acceleration under biphasic conditions was more pronounced (ca. 3- vs 2-fold).

Another important type of experiment is the “non-fluorous control”, in which a catalyst with a non-fluorous ligand is analogously evaluated under monophasic and biphasic conditions. As shown in Figure 2A, 4c gave nearly identical rates in toluene (10 mL, blue diamonds) and toluene/PFMC mixtures (10 mL/5 mL, red squares), consistent with the inability of

Table 1. Polymerization and Polyethylene (PE) Data^a

entry	cat.	solvent system	TOF ($\times 10^{-5}$ g PE/ mol Ni·h) ^b		M_w ($\times 10^{-3}$ g/mol)	M_w/M_n	branches/1000C ^d	crystallinity (%) ^e	T_m (°C, DSC)
			30 min	60 min ^c					
1	4a	toluene	1.89	1.91	234	2.4	4	57	130
2	4a	toluene/PFMC	3.63	3.37	271	2.6	4	52	130
3	4a	toluene/FC-75	2.26	1.69	259	2.9	4	57	131
4	4b	toluene	2.60	2.61	254	3.6	4	49	131
5	4b	toluene/PFMC	3.59	3.61	250	2.7	5	57	130
6	4c	toluene	0.37	0.40	160	2.8	4	55	132
7	4c	toluene/PFMC	0.34	0.33	151	3.0	4	63	131
8	2	toluene	0.88	0.80	180	2.7	5	62	129

^aReaction conditions: ~ 0.010 g of catalyst, room temperature, 100 psig ethylene, 10.0 mL of toluene with/without 5.0 mL of fluorosolvent. ^bTOF values are often expressed in terms of the PE isolated at the end of the reaction. Since the ethylene uptake rates available in this study provide direct TOF measurements, data derived from isolated PE are not analyzed, but would be as follows ($\times 10^{-5}$ g PE/mol Ni·h, entries 1–8): 1.45, 3.02, 1.09, 1.33, 2.06, 0.64, 0.54, 1.02. ^cThe principal difference between the TOF values obtained after 30 and 60 min involves entry 3, the only polymerization to slow during the reaction. ^dAssayed by $^{13}\text{C}\{^1\text{H}\}$ NMR as described in ref 4c. ^eCalculated from the DSC value for ΔH_m based upon 293 J/g for 100% crystallinity as described in ref 4c.

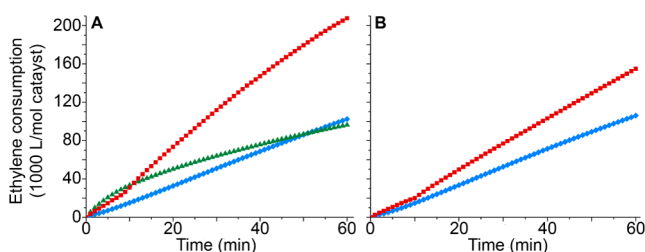


Figure 1. Rates of ethylene polymerization (rt, 8 atm constant pressure). (A) Using 4a: blue diamonds, toluene (10.0 mL); red squares, toluene/PFMC (10.0 mL/5.0 mL); green triangles, toluene/FC-75 (10.0 mL/5.0 mL). (B) Using 4b: blue diamonds, toluene (10.0 mL); red squares, toluene/PFMC (10.0 mL/5.0 mL).

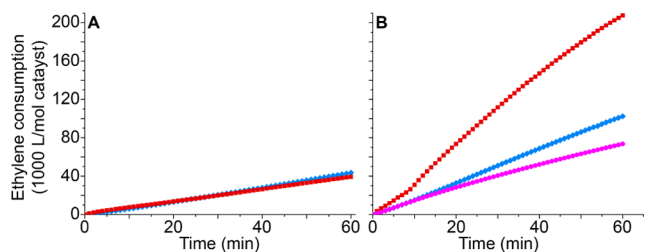


Figure 2. Rates of ethylene polymerization (rt, 8 atm constant pressure). (A) Using 4c: blue diamonds, toluene (10.0 mL); red squares, toluene/PFMC (10.0 mL/5.0 mL). (B) Violet circles, using 2 and toluene (10.0 mL); blue diamonds, using 4a and toluene (10.0 mL, repeat from Figure 1A); red squares, using 4a and toluene/PFMC (10.0 mL/5.0 mL, repeat from Figure 1A).

PPh_3 to partition into the fluorosolvent phase. This also represents the slowest of all catalysts examined in this study.

We next sought to compare the activities of the new fluorosolvent catalysts with those of established systems. Accordingly, Figure 2B superimposes the data obtained with catalyst 2 (Scheme 1) under monophasic conditions (toluene, 10 mL, violet circles) with those for 4a under monophasic (blue diamonds) and toluene/PFMC biphasic (red squares) conditions in Figure 1A. In both cases, the fluorosolvent catalyst is more reactive, and the same trend is apparent with 4b. Grubbs has previously shown that 2 exhibits an activity comparable to those of “classical” metallocenes, such as $[\text{Cp}_2\text{ZrMe}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$,^{1a} thus providing an impressive lower bound for 4a,b.

Table 1 summarizes the TOF values after 30 and 60 min for all of the preceding polymerizations. TOF values based upon isolated polyethylene and total reaction times—a common literature format^{1,2,5} but a less direct measure than ethylene uptake—are provided in the footnotes. These data place 4a,b in the top tier of single-component nickel(II) ethylene polymerization catalysts. Note that, due to the curvature in the ethylene uptake when 4a is used in toluene/FC-75 (Figure 1A), this TOF is a stronger function of time (entry 3, Table 1). The physical characteristics of the polyethylene obtained with 4a,b are only modestly affected by fluorosolvent cosolvents. They fall within previously observed ranges for high-density polyethylene. The dispersities ($M_w/M_n = 2.42\text{--}3.56$) and branch content (4–5 per 1000 carbon atoms) are low, and comparable to those found earlier using 2.^{1a} The melting temperatures (T_m) and crystallinities fall into narrow ranges (130–131 °C; 49–57%) that have abundant precedent.

Some conceptually related results from the Mecking laboratory deserve emphasis.^{4b} This group has prepared analogues of IV (Scheme 1) with water-soluble phosphine ligands in place of pyridine. Such catalysts would be attractive candidates for phase-transfer activation under aqueous/organic liquid/liquid biphasic conditions. However, Mecking has reported that polymerization rates in water can be much faster than those in toluene, presumably because the ligand-free, active nickel catalyst becomes entrained in a lipophilic polymer phase, inhibiting re-association of the hydrophilic ligand. This could be viewed as a variation on liquid/solid phase-transfer activation,⁸ in which the solid phase is not introduced at the outset but rather forms during the reaction. Finally, there have been previous reports of fluorosolvent nickel(II) catalysts for α -olefin oligomerization, but these were concerned with catalyst immobilization or recovery, and activators were required to obtain significant rates.¹⁴

In summary, this study has extended the concept of phase-transfer activation to a new class of metal catalysts, nickel salicylaldehyde complexes with fluorosolvent phosphine ligands. These rank with the most active single-component ethylene polymerization catalysts under organic monophasic conditions, and become significantly more reactive under fluorosolvent/organic liquid/liquid biphasic conditions. Hence, there is a realistic chance that the protocols reported herein, or variants with related catalyst ligand sets or fluorosolvent solid phases—which

often perform as well as liquid phases in biphasic chemistry¹⁵— may find practical application.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b06562.

Experimental procedures and representative NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) (a) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Freidrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460–462. (b) Connor, E. F.; Younkin, T. R.; Henderson, J. I.; Waltman, A. W.; Grubbs, R. H. *Chem. Commun.* **2003**, 2272–2273. (c) Connor, E. F.; Younkin, T. R.; Henderson, J. I.; Hwang, S.; Grubbs, R. H.; Roberts, W. P.; Litzau, J. J. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2842–2854.
- (2) (a) Hicks, F. A.; Jenkins, J. C.; Brookhart, M. *Organometallics* **2003**, *22*, 3533–3545. (b) Jenkins, J. C.; Brookhart, M. *J. Am. Chem. Soc.* **2004**, *126*, 5827–5842. (c) Chen, Z.; Mesgar, M.; White, P. S.; Daugulis, O.; Brookhart, M. *ACS Catal.* **2015**, *5*, 631–636.
- (3) (a) Starzewski, K. A. O.; Witte, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 63–64; *Angew. Chem.* **1987**, *99*, 76–77; (b) Johnson, L. K.; Bennett, A. M.; Ittel, S. D.; Wang, L.; Parthasarathy, A.; Hauptman, E.; Simpson, R. D.; Feldman, J.; Coughlin, E. B. Patent WO 98/30609, 1998; *Chem. Abstr.* **1998**, *129*, 149362.
- (4) (a) Zuideveld, M. A.; Wehrmann, P.; Röhr, C.; Mecking, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 869–873; *Angew. Chem.* **2004**, *116*, 887–891. (b) Göttker-Schnetmann, I.; Korthals, B.; Mecking, S. *J. Am. Chem. Soc.* **2006**, *128*, 7708–7709. (c) Göttker-Schnetmann, I.; Wehrmann, P.; Röhr, C.; Mecking, S. *Organometallics* **2007**, *26*, 2348–2362. (d) Osichow, A.; Rabe, C.; Vogtt, K.; Narayanan, T.; Harnau, L.; Drechsler, M.; Ballauff, M.; Mecking, S. *J. Am. Chem. Soc.* **2013**, *135*, 11645–11650.
- (5) (a) Song, D.-P.; Wu, J.-Q.; Ye, W.-P.; Mu, H.-L.; Li, Y. S. *Organometallics* **2010**, *29*, 2306–2314. (b) Mu, H.-L.; Ye, W.-P.; Song, D.-P.; Li, Y.-S. *Organometallics* **2010**, *29*, 6282–6290. (c) Song, D.-P.; Shi, X.-C.; Wang, Y.-X.; Yang, J.-X.; Li, Y.-S. *Organometallics* **2012**, *31*, 966–975.
- (6) (a) Correa da Costa, R.; Gladysz, J. A. *Chem. Commun.* **2006**, 2619–2621. (b) Correa da Costa, R.; Gladysz, J. A. *Adv. Synth. Catal.* **2007**, *349*, 243–254. (c) Tuba, R.; Correa da Costa, R.; Bazzi, H. S.; Gladysz, J. A. *ACS Catal.* **2012**, *2*, 155–162.
- (7) Xi, Z.; Bazzi, H. S.; Gladysz, J. A. *Org. Lett.* **2011**, *13*, 6188–6191.
- (8) Xi, Z.; Bazzi, H. S.; Gladysz, J. *Catal. Sci. Technol.* **2014**, *4*, 4178–4182.
- (9) (a) *Handbook of Fluorous Chemistry*; Gladysz, J. A., Curran, D. P., Horváth, I. T., Eds.; Wiley/VCH: Weinheim, 2004. (b) *Fluorous Chemistry*; Horváth, I. T., Ed.; Topics in Current Chemistry **308**; Springer: Heidelberg, 2012.

(10) (a) Soós, T.; Bennett, B. L.; Rutherford, D.; Barthel-Rosa, L. P.; Gladysz, J. A. *Organometallics* **2001**, *20*, 3079–3086. (b) Darses, S.; Pucheault, M.; Genêt, J.-P. *Eur. J. Org. Chem.* **2001**, *2001*, 1121–1128.

(11) For partition coefficients of **3a** involving other fluorinated solvents and more polar organic solvents (all >99.9:<0.1), see: Chu, Q.; Yu, M. S.; Curran, D. P. *Tetrahedron* **2007**, *63*, 9890–9895 (Table 6).

(12) Richter, B.; Deelman, B.-J.; van Koten, G. *J. Mol. Catal. A: Chem.* **1999**, *145*, 317–321 (see footnote 2; taken as concentration ratio of <0.14/25:1 or <0.0056:1).

(13) Gladysz, J. A.; Emnet, C. In *Handbook of Fluorous Chemistry*; Gladysz, J. A., Curran, D. P., Horváth, I. T., Eds.; Wiley/VCH: Weinheim, 2004; Ch. 3.

(14) (a) Keim, W.; Vogt, M.; Wasserscheid, P.; Drießen-Hölscher, B. *J. Mol. Catal. A: Chem.* **1999**, *139*, 171–175. (b) Benvenuti, F.; Carlini, C.; Marchionna, M.; Galletti, A. M. R.; Sbrana, G. *J. Mol. Catal. A: Chem.* **2002**, *178*, 9–20.

(15) Gladysz, J. A. In *Handbook of Green Chemistry*; Anastas, P., Ed.; Vol. 1, Homogeneous Catalysis; Crabtree, R. H., Vol. Ed.; Wiley/VCH: Weinheim, 2009; Ch. 2.