1

Introduction: Carbon Monoxide as Synthon in Organic Synthesis

Bartolo Gabriele

University of Calabria, Laboratory of Industrial and Synthetic Organic Chemistry (LISOC), Department of Chemistry and Chemical Technologies, Via Pietro Bucci 12/C, 87036 Arcavacata di Rende, Italy

This book discusses the synthesis of carbonylated compounds by introducing the carbonyl function into an organic substrate (carbonylation) employing the simplest C-1 unit as carbonylating agent, carbon monoxide. Carbon monoxide is a largely available feedstock. It is produced industrially by partial oxidation of petroleum hydrocarbons and steam reforming of light hydrocarbons (including natural gas) or gasification of coal to give syngas (CO and H_2) [1]. In the future, it is expected that a growing amount of carbon monoxide will be available from renewable feedstocks, such as biowastes and CO_2 [2]. CO is also the simplest unit that, upon insertion into an organic substrate, can be directly transformed, without atom loss, into a carbonyl group. It is therefore a desirable and useful building block in synthesis to produce high value-added industrially relevant molecules and fine chemicals.

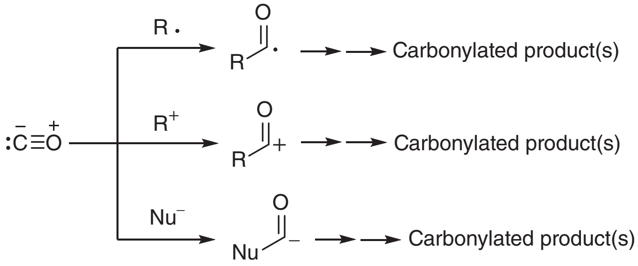
Carbonylation reactions were disclosed in the 1930s by the seminal works of Roelen [3] and Reppe [4] (who also coined the term “carbonylation”) for industrial applications. Since then, the scientific progress in this field has been enormous, thanks, in particular, to the development of more and more selective and efficient catalysts. These catalysts are able to promote a plethora of carbonylations under mild conditions, which can be applied to a large variety of organic substrates. Accordingly, carbonylations with CO have become increasingly more and more important, at the industrial and academic level, as testified by the considerable number of books [5–12] and reviews [13–115] dedicated to this topic and by the increasing number of industrial patents and scientific publications.

As said above, the *incorporation of carbon monoxide into an organic substrate* to give a carbonyl compound is called *carbonylation*. Interestingly, during the last years, considerable effort has been made by the scientific community to use CO surrogates as indirect carbonylating agents or as *in situ* sources of CO (both in industry and in academia, to avoid the direct handling of gaseous and toxic CO). In this book, several representative examples of CO surrogates will also be presented and discussed. Although CO surrogates can be interesting from a practical point of view, it should

Carbon Monoxide in Organic Synthesis: Carbonylation Chemistry,
First Edition. Edited by Bartolo Gabriele.

still be considered that carbon monoxide is cheaper than its surrogates and that carbonylations with CO occur with a higher atom economy.

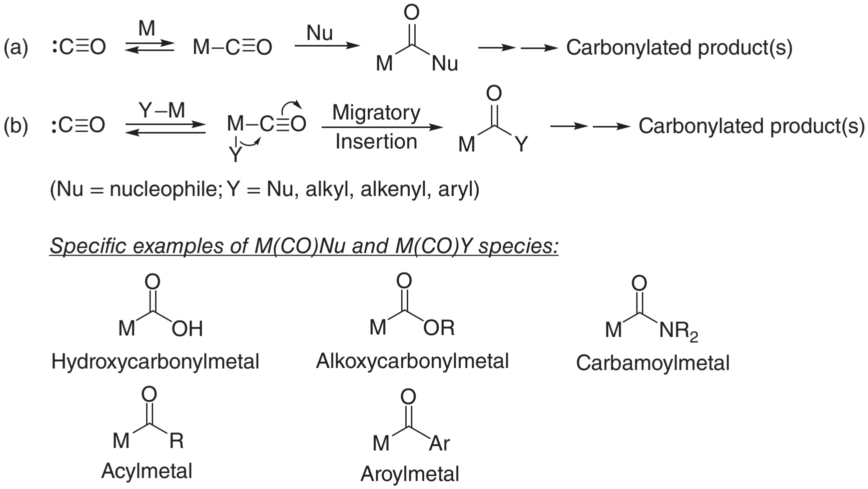
Carbon monoxide possesses the strongest bond currently known (257.3 kcal/mol) [116]. This bond is only weakly polarized in the direction of carbon (the experimental dipole moment is 0.122 D) [117]. These characteristics make carbon monoxide a relatively stable and inert molecule. Consequently, CO can be attacked by highly reactive species, such as free radicals, carbocations, and strong nucleophiles (like alkoxides, amide anions, and organolithium reagents) (Scheme 1.1). These reactions form acyl radicals, acyl carbocations, and $[NuCO]^-$ intermediates (alkoxycarbonyl anions, carbamoyl anions, and acyl anions). They evolve toward forming the final carbonylation product depending on the nature of reactants and reaction conditions (Scheme 1.1).



Scheme 1.1 Reactions of carbon monoxide with free radicals, carbocations, or strong nucleophiles (such as RO^-, R_2N^-, RLi).

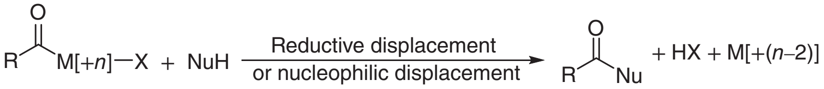
However, the most common way to activate CO in carbonylation reactions under relatively mild conditions is metal coordination. In fact, upon coordination to a metal center M, the carbon atom becomes more electrophilic. It accordingly becomes susceptible to attack even by a relatively weak nucleophile, either external or coordinated to the metal (Scheme 1.2; formal charges are omitted for clarity). When occurring within the coordination sphere of the metal, this process is called *migratory insertion*. In this case, the metal also favors the attack to coordinated CO for entropic reasons. In either case (external attack, Scheme 1.2a, or migratory insertion, Scheme 1.2b), the coordinated carbon monoxide is transformed into a species in which the carbonyl group is bonded to M, and whose particular structure depends, apart from the metal, on the nature of the nucleophile. Thus, if the nucleophilic species is a carbon group (alkyl, alkenyl, or aryl) σ-bonded to the metal undergoing migratory insertion, an acyl- or aroyl-metal species is formed. On the other hand, oxygen and nitrogen nucleophiles will lead to hydroxycarbonyl-, alkoxycarbonyl-, or carbamoyl-metal complexes, respectively (Scheme 1.2).

These intermediates' fate will depend on the nature of the metal and of the reactants taking part in the carbonylation process and on reaction conditions. In most cases, the final carbonylated organic product is formed with the release of the metal, either in its original or in a different oxidation state. In the first case, a catalytic cycle is directly attained. In contrast, in the second case, the metal species must be reported in its original oxidation state (using a suitable redox agent) to achieve a catalytic process. For example, an acyl- or aroyl-metal intermediate R(CO)–M[+*n*]–X



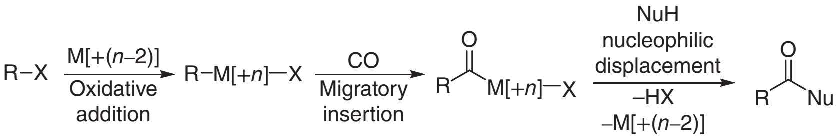
Scheme 1.2 Carbon monoxide coordinated to a metal center becomes more susceptible to nucleophilic attack, either intermolecularly (a) or intramolecularly (*migratory insertion*) (b).

(X^- = halide or other ligands, with M in the oxidation state [+*n*]) may undergo a nucleophilic attack by a nucleophile NuH (like water, alcohol, or an amine), with the formation of the carbonylated product R(CO)Nu (such as a carboxylic acid, an ester, or an amide), HX, and the reduced metal M[+(*n*–2)] (reductive displacement or nucleophilic displacement; Scheme 1.3).



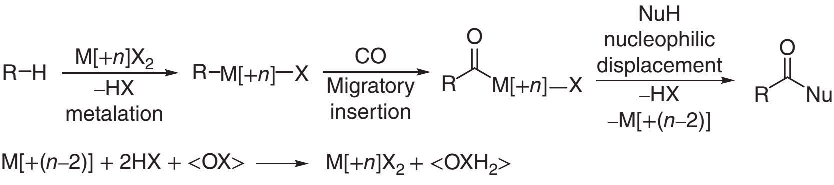
Scheme 1.3 An acyl- or aroyl-metal intermediate (R = carbon group) undergoing reductive displacement (also called nucleophilic displacement).

If the metal initiated the process in its [+(*n*–2)] oxidation state (for example, by oxidative addition of R–X to the metal center to give R–M[+*n*]–X followed by CO migratory insertion), a catalytic cycle is directly achieved (Scheme 1.4). On the other hand, if the metal initiated the process in its [+*n*] oxidation state (for example, by metalation of R–H by M[+*n*]X_2 with the formation of R–M[+*n*]–X + HX, followed by CO migratory insertion), the use of a suitable external oxidant is necessary to reconvert the reduced metal M[+(*n*–2)] to M[+*n*] and realize a catalytic process



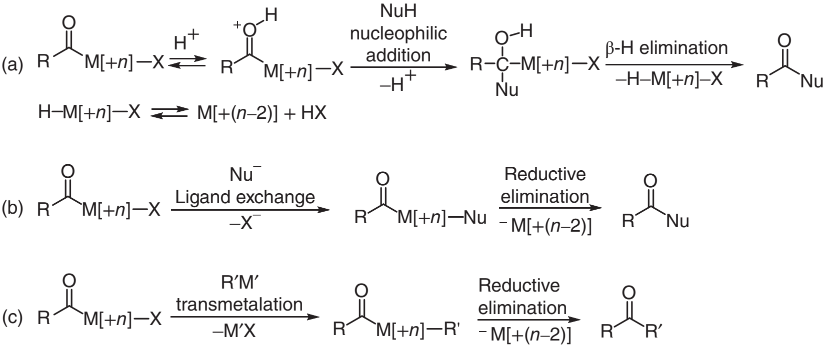
Scheme 1.4 An example of catalytic carbonylation process in which the metal is eliminated at the end of the process in its original oxidation state.

(Scheme 1.5). Clearly, from a practical and economical point of view, the occurrence of a carbonylative catalytic cycle is highly desirable. In the last decades, there has been considerable attention to developing more and more robust and efficient metal catalysts, also heterogeneous and/or with the possibility of being effectively recycled.



Scheme 1.5 An example of catalytic carbonylation process in which the metal is reduced at the end of the process and is reoxidized to its original oxidation state by the action of an external oxidant.

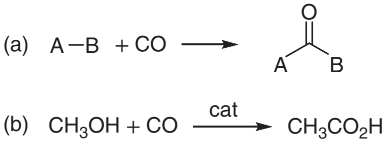
The nucleophilic attack of NuH to an acyl- or aroyl-metal intermediate (either inter- or intramolecular) is a common and important process by which the final carbonylated compound is delivered in a carbonylation reaction. This process is called *reductive displacement* or *nucleophilic displacement*. The exact mechanism this step may take place depends on reaction conditions, and, in particular, if the carbonylation process is done under acidic, neutral, or basic conditions. Under acidic and neutral conditions, the nucleophile tends to attack the carbonyl (possibly protonated) of the R(CO)–M[+*n*]–X complex, with the formation of a tetrahedral intermediate. This intermediate undergoes β-H elimination from the H–O–C–MX moiety to give R(CO)Nu and a metal hydride species H–M[+*n*]–X, in equilibrium with M[+(*n*−2)] + HX (*addition–elimination mechanism*, Scheme 1.6a). On the other hand, under basic conditions, NuH (possibly in its anionic Nu^- form) preferably attacks the metal center, with formal elimination of X^- and formation



Scheme 1.6 Possible mechanistic pathways in the nucleophilic displacement step: (a) nucleophilic attack to the carbonyl followed by β-H elimination from the H–O–C–MX unit (*addition–elimination mechanism*); (b) nucleophilic attack to the metal center followed by reductive elimination (*ligand exchange mechanism*); (c) reaction with an organometallic reagent R′M′ followed by reductive elimination (*transmetalation mechanism*).

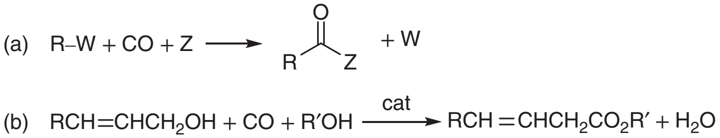
of the R(CO)–M[+*n*]–Nu complex. Reductive elimination then leads to R(CO)Nu and M[+(*n*–2)] (*ligand exchange mechanism*; Scheme 1.6b). This latter case also occurs when the R(CO)–M[+*n*]–X species is attacked by an organometallic reagent R′M′ with the formation of M′X and R(CO)–M[+*n*]–R′ that undergoes reductive elimination to give R(CO)R′ (as occurs in the so-called carbonylative cross-coupling reactions) (*transmetalation mechanism*; Scheme 1.6c).

Depending on the exact stoichiometry of the process, carbonylations can be broadly classified into *direct*, *substitutive*, *additive*, *oxidative*, and *reductive carbonylations*. In *direct carbonylation*, carbon monoxide is formally inserted into an A—B bond of an organic substrate to give a carbonylated product bearing the A(CO)B functionality (Scheme 1.7a). An example is the direct catalytic carbonylation of methanol to acetic acid (Scheme 1.7b), a particularly important industrial process.



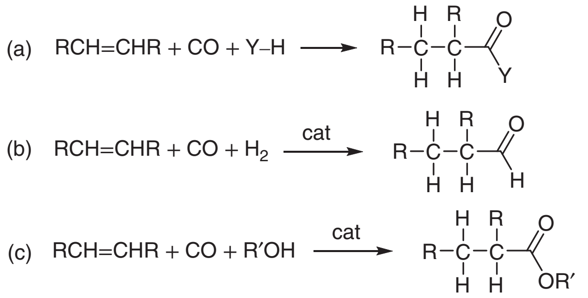
Scheme 1.7 A generic direct carbonylation process (a) and direct carbonylation of methanol to acetic acid (b).

On the other hand, *substitutive carbonylation* corresponds to the formal substitution of a certain functional group W of an organic substrate with a carbonylic functional group (CO)Z (Scheme 1.8a). An example is given by the substitutive carbonylation of an allyl alcohol RCH=CHCH$_2$OH carried out with CO and an alcohol (R′OH) to give a β,γ-unsaturated ester with water as coproduct, as shown in Scheme 1.8b.



Scheme 1.8 A generic substitutive carbonylation process (a) and substitutive carbonylation of allyl alcohols to β,γ-unsaturated esters (b).

Additive carbonylation is a process in which carbon monoxide, together with an H–Y species (Y = hydrogen or a nucleophilic group), adds to an unsaturated carbon–carbon bond, as exemplified in Scheme 1.9a for the double bond. Examples are given by the hydroformylation of olefins (in which Y = H, with the formal addition to the double bond of a hydrogen atom on one carbon and the formyl group on the other one, Scheme 1.9b) or the Reppe alkoxycarbonylation of an olefin with CO and an alcohol (Y = OR′, with the formal addition to the double bond of a hydrogen atom on one carbon and the alkoxycarbonyl group on the other one, Scheme 1.9c).



Scheme 1.9 A generic additive carbonylation process for an olefin (a), additive carbonylation of an olefin with H_2 (hydroformylation) (b), and additive carbonylation of an olefin with an alcohol (Reppe carbonylation) (c).

In an oxidative carbonylation reaction, the process occurs with the formal simultaneous elimination of molecular hydrogen from the substrate(s) (Scheme 1.10a). Although a few examples are known in the literature in which molecular hydrogen is indeed formed as the reaction coproduct, in the majority of the cases, the process, promoted by a metal catalyst M[+n], occurs with simultaneous reduction of the metal by two units and with the concomitant formation of 2 mol of H^+ (Scheme 1.10b). A process like this is not catalytic unless a suitable external oxidant (able to reconvert the reduced metal into its original oxidation state, Scheme 1.10c) is added among the reactants (Scheme 1.10d). An example is the PdI_2-catalyzed oxidative dialkoxycarbonylation of alkynes to give maleic diesters carried out with molecular oxygen as the external oxidant, as shown in Scheme 1.11.

$$\text{(a)}\quad SH_2 + CO \longrightarrow S(CO) + H_2$$

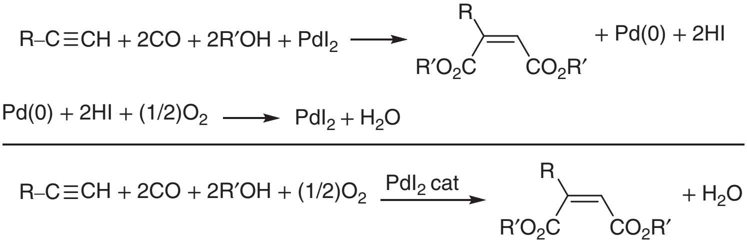
$$\text{(b)}\quad SH_2 + CO + M[+n] \longrightarrow S(CO) + M[+(n{-}2)] + 2H^+$$

$$\text{(c)}\quad M[+(n{-}2)] + 2H^+ + \langle OX\rangle \longrightarrow M[+n] + \langle OXH_2\rangle$$

$$\text{(d)}\quad SH_2 + CO + \langle OX\rangle \xrightarrow{M[+n]\ \text{cat}} S(CO) + \langle OXH_2\rangle$$

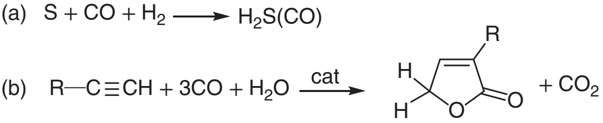
Scheme 1.10 A generic oxidative carbonylation process (a) with the elimination of molecular hydrogen from substrate(s) SH_2 and formation of carbonylated product(s) S(CO) or (b) with reduction by two units of a metal species promoting the process or (d) carried out in the presence of an external oxidant, able to reconvert the promoting metal in its original oxidation state (c). The combination between the stoichiometric process (b) with metal reoxidation (c) gives the reaction (d) catalytic in the metal.

On the other hand, *reductive carbonylation* is when molecular hydrogen is formally inserted together with CO into the organic reactant(s) (Scheme 1.12a). The hydroformylation reaction of olefins, shown in Scheme 1.9b, is the most important example in which molecular hydrogen is used as a coreactant. A more complex example is given by the reductive carbonylation of alkynes, in which molecular hydrogen is formally released from the water-shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$)



Scheme 1.11 PdI_2-catalyzed oxidative dialkoxycarbonylation of alkynes to maleic diesters. The catalytic process is the result of the combination between the dialkoxycarbonylation process occurring with reduction of PdI_2 to Pd(0) followed by reoxidation of Pd(0) to PdI_2 by the action of the external oxidant (molecular oxygen).

and reduces one carbonyl unit into a $-CH_2O-$ moiety within the final unsaturated γ-lactone ring (Scheme 1.12b).



Scheme 1.12 (a) A generic reductive carbonylation process with molecular hydrogen as reducing agent and (b) reductive carbonylation of alkynes to furan-2(5*H*)-ones (in which H_2 is formally produced *in situ* by the water-shift reaction, $CO + H_2O \rightarrow CO_2 + H_2$).

The major emphasis of the book is based on the increasing importance and versatility of transition metal-catalyzed carbonylation processes. The book represents the first attempt to present carbonylations based on the kind of metal promoting the carbonylation process rather than on the carbonylation process type or the carbonylated product's nature. Part I of the book deals with carbonylations promoted by first-row transition metal catalysts (cobalt, nickel, manganese, iron, copper). Part II describes carbonylations promoted by second-row transition metal catalysts (ruthenium, rhodium, palladium, other second-row metals). Carbonylation promoted by third-row transition metal catalysts is discussed in Part III. Chapter 11 is also devoted to metal-free carbonylation processes.

References

1 Reimert, R., Marschner, F., Renner, H.-J., Boll, W., Supp, E., Brejc, M., Liebner, W., and Schaub, G. (2011). Gas production, 2. In: *Ullmann's Encyclopedia of Industrial Chemistry* (eds. H. Baltes, W. Göpel and J. Hesse), 423–479. Weinheim, Germany: Wiley-VCH.

2 Karl, J. and Pröll, T. (2018). *Renewable Sustainable Energy Rev.* 98: 64–78.

3 Roelen, O. (Rührchemie AG) (1938). Verfahren zur Herstellung von sauerstoffhaltigen Verbindungen. German Patent 849548, filed 20 September 1938 and issued 15 September 1952.

4 Reppe, W. (IG Farben) (1939). Verfahren zur Herstellung von Acrylsaeure oder ihren Substitutionserzeugnissen. German Patent 855110, filed 02 August 1939 and issued 10 November 1952.
5 Falbe, J. (ed.) (1970). *Carbon Monoxide in Organic Synthesis*. Berlin: Springer-Verlag.
6 Falbe, J. (ed.) (1980). *New Syntheses with Carbon Monoxide*. Berlin, Germany: Springer-Verlag.
7 Colquhoun, H.M., Thompson, D.J., and Twigg, M.V. (1991). *Carbonylation – Direct Synthesis of Carbonyl Compounds*. New York, NY: Plenum Press.
8 Beller, M. (ed.) (2006). Catalytic carbonylation reactions. In: *Topics in Organometallic Chemistry*, vol. 18, 1–272. Berlin, Germany: Springer.
9 Kollár, L. (ed.) (2008). *Modern Carbonylation Methods*. Weinheim, Germany: Wiley-VCH.
10 Beller, M. and Wu, X.-F. (2013). *Transition Metal Catalyzed Carbonylation Reactions – Carbonylative Activation of C–X Bonds*. Berlin, Germany: Springer.
11 Tambade, P., Bhanage, B., and Patil, Y. (2014). *Studies in Catalytic Carbonylation Reactions*. Riga, Latvia: LAP Lambert Academic Publishing.
12 Wu, X.-F. and Beller, M. (eds.) (2016). Transition metal catalyzed Carbonylative synthesis of heterocycles. In: *Topics in Heterocyclic Chemistry*, vol. 42, 1–166. Berlin: Springer.
13 Ren, Z., Lyu, Y., Song, X., and Ding, Y. (2020). *Appl. Catal., A* 595: 117488.
14 Nogi, K. and Yorimitsu, H. (2020). *Chem. Asian J.* 15: 441–449.
15 Kalck, P., Le Berre, C., and Serp, P. (2020). *Coord. Chem. Rev.* 402, UNSP 213078.
16 Jones, D.J., Lautens, M., and McGlacken, G.P. (2019). *Nat. Catal.* 2: 843–851.
17 Perrone, S., Troisi, L., and Salomone, A. (2019). *Eur. J. Org. Chem.*: 4626–4643.
18 Zhao, S. and Mankad, N.P. (2019). *Catal. Sci. Technol.* 9: 3603–3613.
19 Mancuso, R., Della Ca', N., Veltri, L., Ziccarelli, I., and Gabriele, B. (2019). *Catalysts* 9: 610.
20 Peng, J.-B., Geng, H.-Q., and Wu, X.-F. (2019). *Chem* 5: 526–552.
21 Urban, B., Papp, M., and Skoda-Foldes, R. (2019). *Curr. Green Chem.* 6: 78–95.
22 Ma, K., Martin, B.S., Yin, X., and Dai, M.J. (2019). *Nat. Prod. Rep.* 36: 174–219.
23 Nielsen, D.U., Neumann, K.T., Lindhardt, A.T., and Skrydstrup, T. (2019). *J. Labelled Compd. Radiopharm.* 61: 949–987.
24 Xu, F.N. and Han, W. (2019). *Chin. J. Org. Chem.* 38: 2519–2533.
25 Taddei, C. and Gee, A.D. (2019). *J. Labelled Compd. Radiopharm.* 61: 237–251.
26 Matsubara, H., Kawamoto, T., Fukuyama, T., and Ryu, I. (2018). *Acc. Chem. Res.* 51: 2023–2035.
27 Gabriele, B. (2018). Synthesis of heterocycles by palladium-catalyzed carbonylative reactions. In: *Advances in Transition-Metal Mediated Heterocyclic Synthesis* (eds. D. Solé and I. Fernández), 55–127. London, UK: Academic Press/Elsevier.
28 Gabriele, B. (2018). *Targets in Heterocyclic Systems*, vol. 22 (eds. O.A. Attanasi, P. Merino and D. Spinelli), 41–55. Rome, Italy: Italian Chemical Society.
29 Peng, J.-B. and Wu, X.-F. (2018). *Angew. Chem. Int. Ed.* 57: 1152–1160.
30 Li, Y., Hu, Y., and Wu, X.-F. (2018). *Chem. Soc. Rev.* 47: 172–194.

31 Albano, G. and Aronica, L.A. (2017). *Eur. J. Org. Chem.*: 7204–7221.

32 Piens, N. and D'hooghe, M. (2017). *Eur. J. Org. Chem.*: 5943–5960.

33 Shen, C. and Wu, X.-F. (2017). *Chem. Eur. J.* 23: 2973–2978.

34 Pineiro, M., Dias, L.D., Damas, L., Aquino, G.L.B., Calvete, M.J.F., and Pereira, M.M. (2017). *Inorg. Chim. Acta* 455: 364–377.

35 Peng, J.B., Qi, X., and Wu, X.-F. (2017). *Synlett* 28: 175–194.

36 Feng, J.-B. and Wu, X.-F. (2017). *Adv. Heterocycl. Chem.* 121: 207–246.

37 Zhu, Z., Zhang, W., and Gao, Z. (2016). *Progr. Chem.* 28: 1626–1633.

38 Song, H., Kang, M., Jin, R., Jin, F., and Chen, J. (2016). *Progr. Chem.* 28: 1313–1327.

39 Zoeller, J.R. (2016). *Org. Process Res. Dev.* 20: 1016–1025.

40 Gehrtz, P.H., Hirschbeck, V., Ciszek, B., and Fleischer, I. (2016). *Synthesis* 48: 1573–1596.

41 Friis, S.D., Lindhardt, A.T., and Skrydstrup, T. (2016). *Acc. Chem. Res.* 49: 594–605.

42 Kalck, P. and Urrutigoity, M. (2015). *Inorg. Chim. Acta* 431: 110–121.

43 Rahman, O. (2015). *J. Labelled Compd. Radiopharm.* 58: 86–98.

44 Cavinato, G. and Toniolo, L. (2014). *Molecules* 19: 15116–15161.

45 Fang, W., Zhu, H., Deng, Q., Liu, S., Liu, X., Shen, Y., and Tu, T. (2014). *Synthesis* 46: 1689–1708.

46 Sumino, S., Fusano, A., Fukuyama, T., and Ryu, I. (2014). *Acc. Chem. Res.* 47: 1563–1574.

47 Wu, X.-F., Fang, X., Wu, L., Jackstell, R., Neumann, H., and Beller, M. (2014). *Acc. Chem. Res.* 47: 1041–1053.

48 Kealey, S., Gee, A., and Miller, P.W. (2014). *J. Labelled Compd. Radiopharm.* 57: 195–201.

49 Fukuyama, T., Totoki, T., and Ryu, I. (2014). *Green Chem.* 16: 2042–2050.

50 Wu, L., Fang, X., Liu, Q., Jackstell, Beller, M., and Wu, X.-F. (2014). *ACS Catal.* 4: 2977–2989.

51 Gadge, S.T. and Bhanage, B.M. (2014). *RSC Adv.* 4: 10367–10389.

52 Wu, X.-F., Neumann, H., and Beller, M. (2013). *ChemSusChem* 6: 229–241.

53 Wu, X.-F., Neumann, H., and Beller, M. (2013). *Chem. Rev.* 113: 1–35.

54 Gabriele, B., Mancuso, R., and Salerno, G. (2012). *Eur. J. Org. Chem.*: 6825–6839.

55 Diebolt, O., van Leeuwen, P.W.N.M., and Kamer, P.C.J. (2012). *ACS Catal.* 2: 2357–2370.

56 Fan, Q., Liu, J., Chen, J., and Xia, C. (2012). *Chin. J. Catal.* 33: 1435–1447.

57 Wu, X.-F. and Neumann, H. (2012). *ChemCatChem* 4: 447–458.

58 Liu, Q., Zhang, H., and Lei, A. (2011). *Angew. Chem. Int. Ed.* 50: 10788–10799.

59 Omae, I. (2011). *Coord. Chem. Rev.* 255: 139–160.

60 Occhiato, E.G., Scarpi, D., and Prandi, C. (2010). *Heterocycles* 80: 697–724.

61 Haynes, A. (2010). *Adv. Catal.* 53: 1–45.

62 Liu, J., Chen, J., Sun, W., and Xia, C. (2010). *Chin. J. Catal.* 31: 1–11.

63 Brennführer, A., Neumann, H., and Beller, M. (2009). *ChemCatChem* 1: 28–41.

64 Brennführer, A., Neumann, H., and Beller, M. (2009). *Angew. Chem. Int. Ed.* 48: 4114–4133.

65 Ragaini, F. (2009). *Dalton Trans.*: 6251–6266.

66 Barnard, C.F.J. (2008). *Organometallics* 27: 5402–5422.

67 Chaudhari, R.V. (2008). *Curr. Opin. Drug Discovery Dev.* 11: 820–828.

68 Veige, A.S. (2008). *Polyhedron* 27: 3177–3189.

69 Boyarskii, V.P. (2008). *Russ. J. Gen. Chem.* 78: 1742–1753.

70 Liu, M., Wu, Y., Du, Z, Yuan, H., and Ge, J. (2008). *Chin. J. Catal.* 29: 489–496.

71 Diaz, D.J., Darko, A.K., and McElwee-White, L. (2007). *Eur. J. Org. Chem.*: 4453–4465.

72 Langstom, B., Itsenko, O., and Rahman, O. (2007). *J. Labelled Compd. Radiopharm.* 50: 794–810.

73 Church, T.L., Getzler, Y.D.Y.L., Byrne, C.M., and Coates, G.W. (2007). *Chem. Commun.*: 657–674.

74 Shibata, T. (2006). *Adv. Synth. Catal.* 348: 2328–2336.

75 Vasapollo, G. and Mele, G. (2006). *Curr. Org. Chem.* 10: 1397–1421.

76 Ragaini, F., Cenini, S., Gallo, E., Caselli, A., and Fantauzzi, S. (2006). *Curr. Org. Chem.* 10: 1479–1510.

77 Ungvary, F. (2005). *Coord. Chem. Rev.* 249: 2946–2961.

78 Trzeciak, A.M. and Ziolkowski, J.J. (2005). *Coord. Chem. Rev.* 249: 2308–2322.

79 Muzart, J. (2005). *Tetrahedron* 61: 9423–9463.

80 Park, K.H. and Chung, Y.K. (2005). *Synlett*: 545–559.

81 Gibson, S.E. and Mainolfi, N. (2005). *Angew. Chem. Int. Ed.* 44: 3022–3037.

82 Gabriele, B., Salerno, G., Costa, M., and Chiusoli, G.P. (2004). *Curr. Org. Chem.* 8: 919–946.

83 Vizer, S.A., Yerzhanov, K.B., Al Quntar, A.A.A., and Dembitsky, V.M. (2004). *Tetrahedron* 60: 5499–5538.

84 Green, M.J., Cavell, K.J., Edwards, P.G., Tooze, R.P., Skelton, B.W., and White, A.H. (2004). *Dalton Trans.*: 3251–3260.

85 Thomas, C.M. and Suss-Fink, G. (2004). *Coord. Chem. Rev.* 243: 125–142.

86 Cornils, B. and Herrmann, W.A. (2003). *J. Catal.* 216: 23–31.

87 des Abbayes, H. and Salaun, J.Y. (2003). *Dalton Trans.*: 1041–1052.

88 Gabriele, B., Salerno, G., Costa, M., and Chiusoli, G.P. (2003). *J. Organomet. Chem.* 687: 219–228.

89 Skoda-Foldes, R. and Kollár, L. (2002). *Curr. Org. Chem.* 6: 1097–1119.

90 Kiss, G. (2001). *Chem. Rev.* 101: 3435–3456.

91 del Rio, I., Claver, C., and van Leeuwen, P.W.N.M. (2001). *Eur. J. Inorg. Chem.*: 2719–2738.

92 Bertoux, F., Monflier, E., Castanet, Y., and Mortreux, A. (1999). *J. Mol. Catal. A: Chem.* 143: 11–22.

93 Wender, I. (1996). *Fuel Process. Technol.* 48: 189–297.

94 Ragaini, F. and Cenini, S. (1996). *J. Mol. Catal. A: Chem.* 109: 1–25.

95 Ryu, I. and Sonoda, N. (1996). *Angew. Chem. Int. Ed.* 35: 1050–1066.

96 Beller, M., Cornils, B., Frohning, C.D., and Kohlpaintner, C.W. (1995). *J. Mol. Catal. A: Chem.* 104: 17–85.

97 Khumtaveeporn, K. and Alper, H. (1995). *Acc. Chem. Res.* 28: 414–422.

98 Yamamoto, A. (1995). *Bull. Chem. Soc. Jpn.* 68: 433–446.

99 Tsuji, J. and Mandai, T. (1993). *J. Organomet. Chem.* 451: 15–21.

100 Ford, P.C., Ryba, D.W., and Belt, S.T. (1993). *Adv. Chem.* 238: 27–43.

101 Lin, J.J. and Knifton, J.F. (1992). *Adv. Chem. Ser. D* 230: 235–247.

102 Ojima, A., Zhang, Z., Korda, A., Ingallina, P., and Clos, N. (1992). *Adv. Chem. Ser. D* 230: 277–296.

103 Braca, G., Galletti, A.M.R., Sbrana, G., and Trabuco, E. (1992). *Adv. Chem. Ser. D* 230: 309–322.

104 Moloy, K.G. and Wegman, R.W. (1992). *Adv. Chem. Ser. D* 230: 323–338.

105 Zoeller, J.R., Cloyd, J.D., Lafferty, N.L., Nicely, V.A., Polichnowski, S.W., and Cook, S.L. (1992). *Adv. Chem. Ser. D* 230: 377–394.

106 Oswald, A.A., Hendriksen, D.E., Kastrup, R.V., and Mozeleski, E.J. (1992). *Adv. Chem. Ser. D*: 395–418.

107 Chiusoli, G.P. (1991). *Transition Met. Chem.* 16: 553–564.

108 Iwasaki, M., Ishii, Y., and Hidai, M. (1991). *J. Synth. Org. Chem. Jpn.* 49: 909–918.

109 Jenner, G. (1989). *Appl. Catal.* 50: 99–118.

110 Lapidus, A.L. and Pirozhkov, S.D. (1989). *Usp. Khim.* 58: 197–233.

111 Collin, J. (1988). *Bull. Soc. Chim. Fr.* 6: 976–981.

112 Gulevich, Y.V., Bumagin, N.A., and Beletskaya, I.P. (1988). *Usp. Khim.* 57: 529–561.

113 Chiusoli, G.P. (1987). *Transition Met. Chem.* 12: 89–96.

114 Narayana, C. and Periasamy, M. (1985). *Synthesis*: 253–268.

115 Brown, H.C. (1969). *Acc. Chem. Res.* 2: 65–72.

116 Liu, Y.-R. (2007). *Comprehensive Handbook of Chemical Bond Energies*. Boca Raton, FL: Taylor and Francis.

117 Scuseria, G.E., Miller, M.D., Jensen, F., and Geertsen, J. (1991). *J. Chem. Phys.* 94: 6660–6663.